METHODS OF FORMATION OF THE NITROSO GROUP AND ITS FORMATIONS*

J. H. Boyer

Petroleum Research Fund, American Chemical Society, Washington, D. C. and Chicago Circle Campus, University of Illinois, Chicago, Illinois

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A. Introduction

Appreciation of the chemistry of the C-nitroso group has developed slowly notwithstanding its extensive literature. Undoubtedly a contributing factor has been its absence, except for a few examples, in naturally occurring materials.

In the past decade there have been several important developments including the n.m.r. analysis of the structural relationship between benzfuroxan and o-dinitrosobenzene, the e.s.r. determination of nitroso radical-anions, photochemical nitrosations, deoxygenation to a nitrene and addition to dienes which have brought nitroso chemistry to the forefront.

Organic synthesis has been substantially helped by the chemistry of the C-nitroso function but it would appear that it will be even more richly rewarded in the future. Two examples may serve to illustrate. In the first, addition of the nitroso group to a C-H bond adjacent to an olefinic, azomethine or other unsaturated linkage offers a promising method to be developed for introducing a functional group at an sp^2 carbon atom. The second example consists in the emerging chemistry of the nitroso group conjugated with one or more unsaturated linkages and is demonstrated in conjugate addition and valence isomerization reactions of nitroso olefins and in the recently discovered ethynyl nitroso compounds.

A comprehensive presentation(1)of the chemistry of the C-nitroso compounds appeared recently. The present work is intended to be complementary and to include new information in the rapidly growing field.

B. Preparative Methods

1. Nitric oxide and radicals

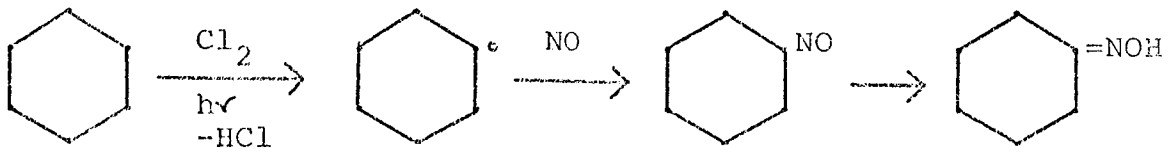
In an early recognition of the affinity between nitric oxide and organic radicals, it was assumed that the appearance of a blue color on mixing triphenylmethyl with nitric oxide in ether in the absence of air denoted the presence of triphenylnitroso-methane (equation 1). Reversibility of the reaction was suggested by the disappearance of the blue color and recovery of starting materials on evaporation of the solvent (2).

$$(C_6H_5)_3C\cdot + NO \rightleftharpoons (C_6H_5)_3CNO \qquad (1)$$

Many reactions which lead to the formation of nitroso compounds are best understood on the basis of a combination of nitric oxide with an appropriate free radical. It is such a combination, for example, which permits nitric oxide to inhibit free radical chain reactions (3). The formation of the lower molecular-weight nitrosoalkanes has been observed in gas-phase reactions between nitric oxide and the corresponding alkyl group generated *in situ* by the photolysis of an azoalkane (4), pyrolysis of a dialkyl mercury compound (5), photolysis of an alkyl halide (6, 7), the addition of a radical such as nitrogen dioxide to an olefin (8) (equation 2), and by other means. It is reported that γ-irradiation of a mixture of carbon tetrachloride and nitric oxide leads to the formation of trichloronitrosomethane (9).

$$CF_2{=}CF_2 \xrightarrow{NO_2} O_2NCF_2CF_2\cdot \xrightarrow{NO} O_2NCF_2CF_2NO \qquad (2)$$

Nitric oxide readily combines with the cyclohexyl radical which may have been generated by the action of a chlorine atom on cyclohexane (10) (equation 3) and with the reactive diradical form of p-xylylene (11) (equation 4).



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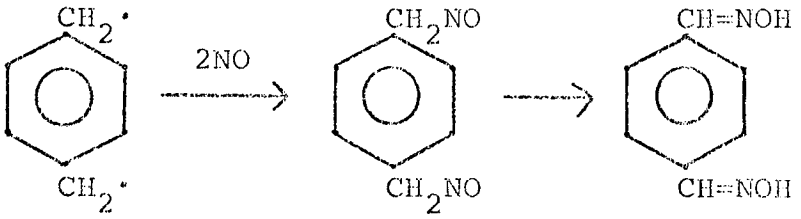


(4)

Nitroso olefins in which the substituent is attached to sp^2 carbon are less well-known; nevertheless perfluoronitrosoethylene has been obtained from the reaction between trifluoroiodoethylene and nitric oxide (12) (equation 5). In contrast trifluoronitrosoethylene has not been detected in the reaction mixture obtained from trifluorochloroethylene and nitric oxide (13) and a reaction presumably initiated by nitrogen dioxide gives saturated products instead. Nitroso olefins with the substituent attached to sp^3 carbon have been prepared in a similar way (14) (equation 6) through irradiation of an allylic iodide in the presence of nitric oxide.

$$CF_2{=}CFI \xrightarrow[h\nu]{NO} CF_2{=}CFNO \qquad (5)$$

$$CF_2{=}CHCH_2I \xrightarrow[h\nu]{NO} CF_2{=}CHCH_2NO \qquad (6)$$

+ other products

Apparently pure nitric oxide does not react with monoolefins under ordinary conditions (15); however, a trace of nitrogen dioxide which is usually present will initiate a reaction leading to a mixture of products in which nitro compounds predominate. From isobutylene up to 45% tris(nitro-t-butyl)hydroxylamine has been reported (16) (equation 7). The transformation of olefins

$$(CH_3)_2C{=}CH_2 \xrightarrow{NO_2} O_2NC_4H_8\cdot \xrightarrow{NO} ONC_4H_8NO_2$$

$$2O_2NC_4H_8\cdot + ONC_4H_8NO_2 \longrightarrow (C_4H_8NO_2)_2NOC_4H_8NO_2 \qquad (7)$$

into nitriles by nitric oxide at high temperatures is not completely understood (17) (equation 8) and the intermediacy of nitroso derivatives has not been established.

$$CH_2{=}CHCH_3 \xrightarrow[\text{argon}]{NO,\ 450^\circ} CH_2{=}CHCN \qquad (8)$$

Carbonyl derivatives with the nitroso group attached to the carbonyl carbon are unknown; however, CH_3CONO has been a suggested

intermediate in the photochemical oxidation of nitric oxide to nitrogen dioxide in acetone (18). The formation of nitroso aromatic compounds by the combination of aryl radicals and nitric oxide apparently has not been reported.

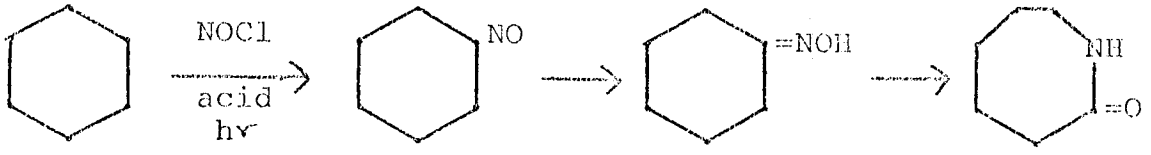
Only a few nitrosoacetylenes in which the substituent is attached to an sp carbon are known, none of which have been obtained in reactions employing nitric oxide. Experiments with bromoacetylene and nitric oxide led to the conclusion that the ethynyl radical ($HC{\equiv}C\cdot \longleftrightarrow \dot{H}C{=}C:$) is unreactive toward nitric oxide (19). Primary products formed are carbon monoxide and cyanogen bromide. An indication that radicals at sp carbon will react with nitric oxide is found in the formation of nitrosyl cyanide on flash photolysis of either cyanogen or cyanogen bromide in the presence of nitric oxide (20) (equation 9) and in the pyrolysis of mercuric cyanide in the presence of nitric oxide (21).

$$BrCN \xrightarrow{h\nu} \cdot CN \xrightarrow{NO} ONCN \qquad (9)$$

2. Irradiation of nitrosyl halides and alkanes

Irradiation of mixtures of saturated aliphatic hydrocarbons and nitrosyl halides will also lead to the formation of corresponding nitrosoparaffins. A mixture of products may be obtained from a hydrocarbon in which hydrogen atoms are not equivalent. The dimer of nitrosocyclohexane has been obtained from cyclohexane and nitrosyl chloride upon irradiation by ultra-violet light (22).

When the reaction, assumed to proceed by the formation and recombination of radicals, is carried out in the presence of strong acid, such as hydrochloric or sulfuric acid or phosphorous oxychloride, the product undergoes isomerization, first to the oxime and then by a Beckman rearrangement into the cyclic amide, caprolactam (23) (equation 10). There is a report that irradiation of a mixture of cyclohexane, benzophenone, concentrated hydrochloric acid and nitric oxide in which oxygen is also present leads to the formation of an unidentified dinitrosocyclohexane (24).



(10)

Irradiation with Co^{60} of cyclohexane solutions containing nitrosyl chloride has also brought about the formation of nitrosocyclohexane (isolated as the isomeric oxime of cyclohexanone) along with cyclohexyl chloride and cyclohexanone (25).

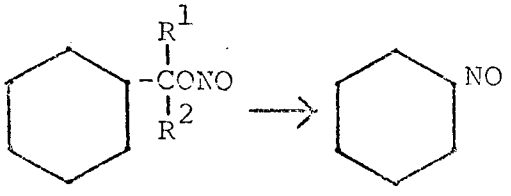
3. Pyrolysis and photolysis of nitrite esters

Pyrolysis or photolysis of a nitrite ester may result in an intramolecular rearrangement by a concerted mechanism or may require a dissociation followed by a recombination. The formation of nitrosomethane and acetone from tert-butyl nitrite by either pyrolysis (26) or photolysis (27)

is satisfactorily accounted for on the basis of initial cleavage into nitric oxide and the trimethylmethoxy radical. The latter then further dissociates into acetone and the methyl radical which combines with nitric oxide (equation 11). Ethane is also

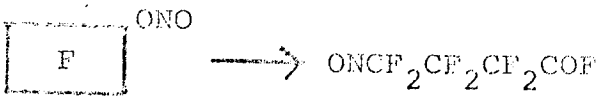
		approximate ΔH (kcal/mols)	
(a)	$(CH_3)_3CONO \longrightarrow (CH_3)_3CO\cdot + NO$	35	
(b)	$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot$	5	
(c)	$(CH_3)_3CONO + CH_3\cdot \longrightarrow (CH_3)_3CO\cdot + CH_3NO$	-30	
(d)	$CH_3\cdot + NO \longrightarrow CH_3NO$	-65	
(e)	$(CH_3)_3CO\cdot + NO \longrightarrow (CH_3)_3CONO$	-35	(11)

produced and its formation supports the intermediacy of methyl radicals. That alkyl radicals may react with nitrites, step (c), is demonstrated in the formation of nitrosomethane from either butyl or amyl nitrite and acetyl peroxide in which the latter must serve as the precursor of the methyl group (28). One of the many preparations for nitrosocyclohexane is based on a similar reaction and demonstrates the expected tendency for the largest of the three alkyl groups which may migrate to become attached to nitrogen (29) (equation 12).



$$+ \quad R^1COR^2 \qquad (12)$$

The pyrolytic ring-opening of perfluorocyclobutyl nitrite has been explained on the basis of initial dissociation into radicals but with the recognition that the reaction could proceed with ionic intermediates or could require an intramolecular concerted mechanism (30) (equation 13). In general cycloalkyl nitrites (ring size of 4 to 7 atoms) photolyse into ω-nitroso aldehydes (31). A similar rearrangement of a suggested intermediate vinyl nitrite has been postulated to account for the photolytic isomerization of 1-phenyl-2-nitropropene (32) (equation 14). A photolytic isomerization of certain nitrobutadienes and aromatic compounds may require a 1,5-migration of the nitroso group (32) (equations 15, 16) from oxygen to carbon.



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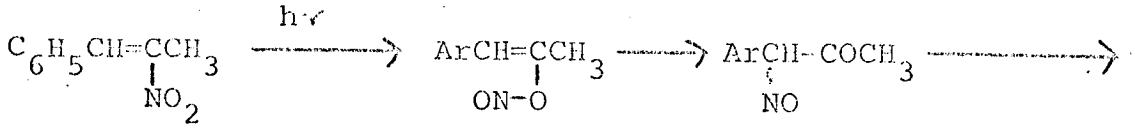

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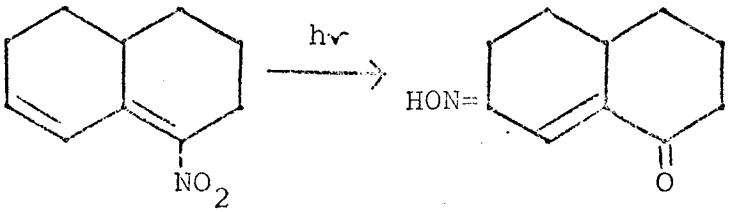

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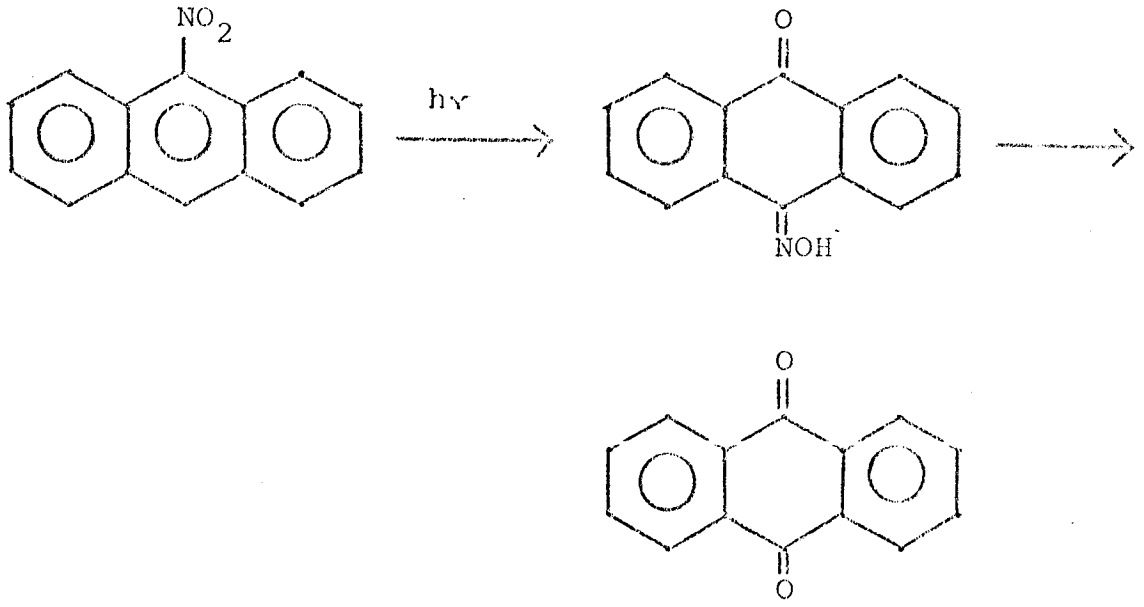
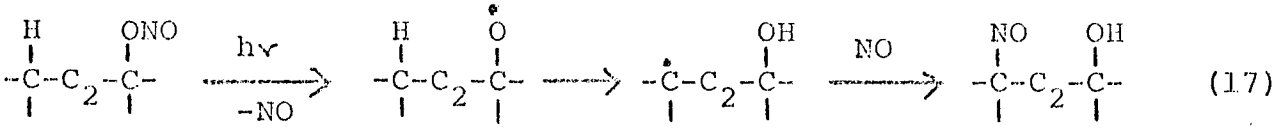


(16)

A 1,5-migration of the nitroso group from oxygen to carbon is a characteristic feature of the Barton reaction, in which alkyl nitrites (with a carbon chain of at least four atoms) may be transformed into 4-nitroso alcohols (33, 34). Evidently a rearrangement of an intermediate alkoxy radical is required (33, 35) (equation 17). It has provided a dramatic synthesis for



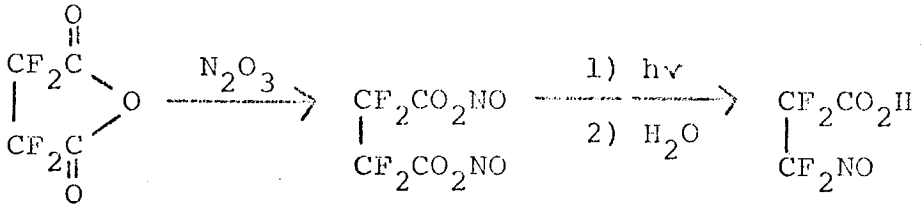
(17)

a number of organic molecules otherwise available only with difficulty. Cycloheptyl nitrite undergoes photolytic isomerization into both 7-nitrosoheptanal and 4-nitrosocycloheptanol (31) but cyclooctyl nitrite gives only the Barton product, 4-nitrosocyclo-octanol (31).

A perfluoro acyl nitrite is available from either the corresponding acid anhydride or silver salt of the carboxylic acid. Trifluoronitrosomethane can be obtained in yields better than fifty percent from the pyrolysis or the photolysis of trifluoroacetyl nitrite (36) (equation 18).. It has also been prepared from silver trifluoroacetate and nitrosyl chloride (37) (equation 19). Each reaction has been extended to perfluoro homologs (38, 39) and to cyclic anhydrides (39) (equation 20).

$$(CF_3CO)_2O \xrightarrow{N_2O_3} CF_3CO_2NO \xrightarrow[\text{or } \triangle]{h\nu} CF_3NO \qquad (18)$$

$$CF_3CO_2Ag \xrightarrow[<-10^{o}]{NOCl} CF_3NO \qquad (19)$$



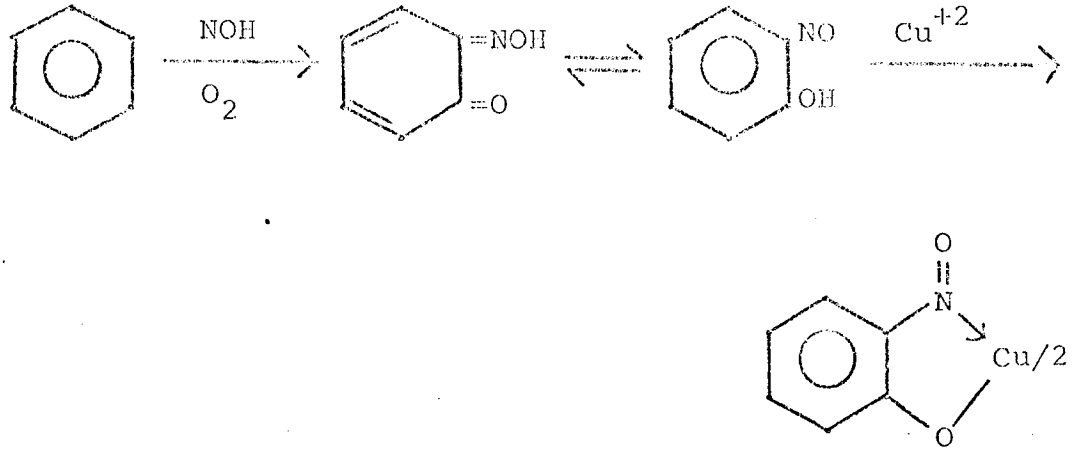
(20)

With or without irradiation nitrosyl chloride reacted explosively with silver trichloroacetate and no product could be identified (40). A successful reaction led to the formation of trichloronitrosomethane from the treatment of the sodium salt of trichlorosulfinate with nitrosyl chloride in a sealed tube at 0^{o} (40) (equation 21).

$$NaO_2SCCl_3 \xrightarrow{NOCl} Cl_3CSO_2NO \longrightarrow Cl_3CNO \qquad (21)$$

4. Oxidative nitrosation (Baudisch reaction)

According to Baudisch, oxidative nitrosation of aromatic compounds proceeds by the simultaneous introduction of the nitroso and hydroxyl group into adjacent positions on the nucleus when treated with nitrosyl hydride and oxygen. Participation of copper salts appears necessary to stabilize the nitrosyl radical and to prevent the formation of <u>para</u> nitrosophenols (41) (equation 22).



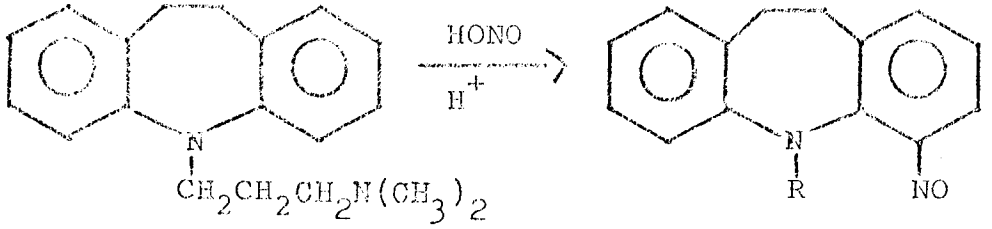
(22)

5. Nitrosation of tertiary aromatic amines

Probably the first known method for nitrosation at carbon consisted in the treatment of certain aromatic tertiary amines with nitrous acid (42). In this way <u>p</u>-nitroso-N,N-dimethylaniline is easily prepared (43). A steric hindrance to the reaction may

be introduced when larger groups are attached either at nitrogen or at the position ortho to the amino function (44). Efforts to achieve dinitrosation have not been successful. Nitrosation of N,N-diphenylmethyl amine gave only the mononitroso derivative, p-nitroso-N-phenyl-N-methylaniline (45). Again only one benzene ring was nitrosated in experiments with N,N'-diethyl-N,N'-diphenyl-2-butene-1,4-diamine (46) (equation 23). The nitroso group is not invariably introduced into the para-position and sometimes an ortho-position is selected (47) (equation 24). In certain examples such

$$C_6H_5NCH_2CH{=}CHCH_2NC_6H_5 \xrightarrow[H^+]{HONO} C_6H_5NCH_2CH{=}CHCH_2NC_6H_4NO\text{-}p \qquad (23)$$



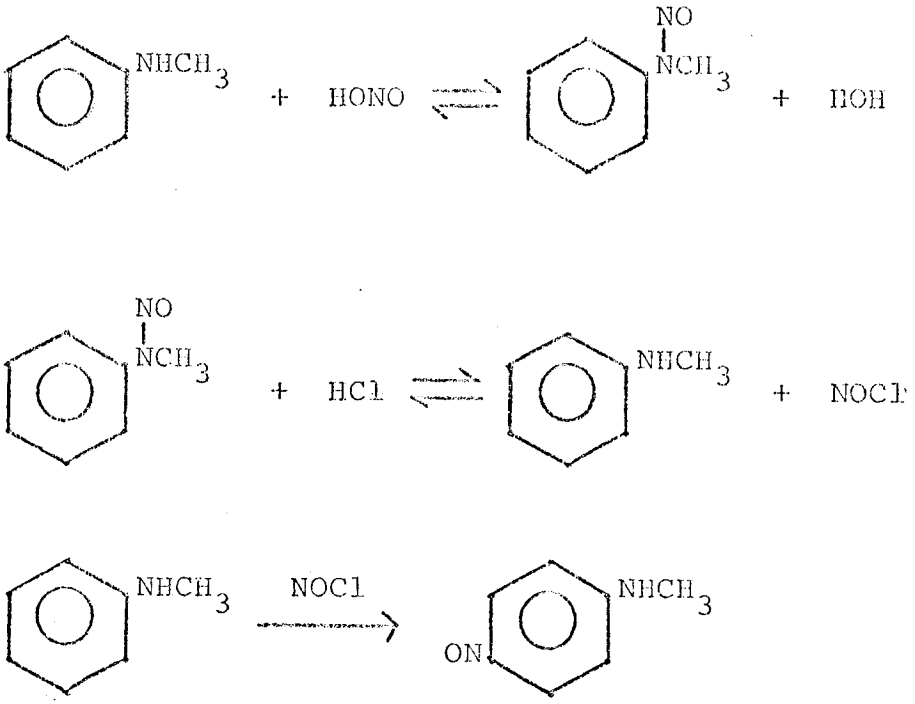
(24)

as p-benzyl-N,N-dimethylaniline where the para-position is already occupied, nitrosation presumably occurs ortho to the amine function (48).

6. Nitrosation of secondary aromatic amines

a. Fischer-Hepp reaction. Nitrosation of secondary aromatic amines generally occurs initially at nitrogen and is reversible. In hydrochloric or hydrobromic acid the N-nitroso compound rearranges to the para-nitroso isomer. The isomerization, known

as the Fischer-Hepp reaction, proceeds intermolecularly with the intermediate formation of nitrosyl chloride followed by nitrosation generally at the para-position (49) (equation 25). Denitrosation of an aromatic N-nitrosamine appears to be more rapid in hydrochloric acid than it is in sulfuric acid (50), in agreement with low yields for the isomerization step when carried out in sulfuric acid (49). This suggests that nuclear



(25)

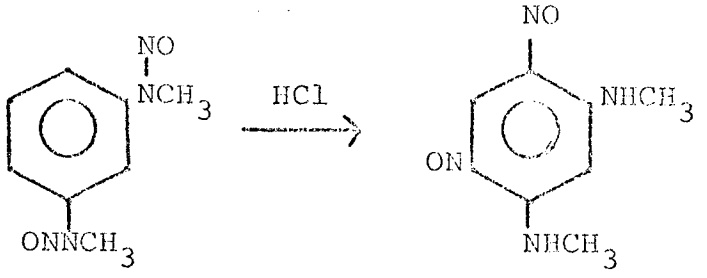
nitrosation occurs directly when certain secondary aromatic amines are appropriately treated in concentrated sulfuric acid. The reaction does not occur in nitric acid (51).

The intermediate formation of nitrosyl chloride in the Fischer-Hepp reaction was demonstrated in the formation of the

nitrosyl chloride adduct of anethole when the latter was present during the treatment of N-nitroso-N-methyl aniline with alcoholic hydrogen chloride in ether (49).

Nitrosation in the ring may be hindered when the para position is occupied by another substituent (49) or by large substituents on the amine nitrogen (51). Poor yields of p-nitroso N-n-hexylaniline were obtained from the N-nitroso isomer and the corresponding N-octyl analog was not transformed into its para-nitroso isomer (51).

A particularly interesting example of the Fischer-Hepp reaction is found in the isomerization of the N,N'-dinitroso-N,N'-dimethyl derivative of m-phenylenediamine (52) (equation 26).

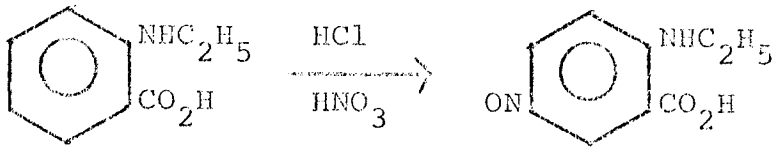


(26)

The reaction proceeds smoothly to transform secondary N-nitroso-α-naphthylamines into the expected 4-nitroso isomers (49); but N-nitroso-1-bromo-2-methylamino-naphthalene does not undergo the Fischer-Hepp reaction.

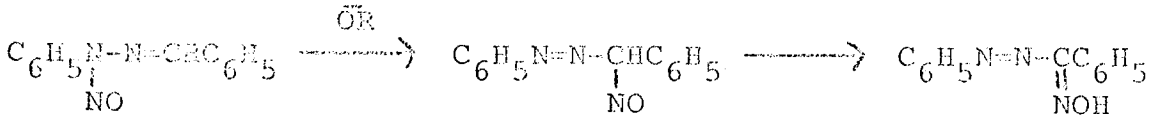
A few secondary amines have been nitrosated by nitric acid in the presence of hydrochloric acid. The addition of sodium nitrate to fuming hydrochloric acid containing N-ethylanthranilic

acid transforms the latter into its p-nitroso derivative (53) (equation 27). From its reaction with nitric acid in alcoholic hydrogen chloride, p-acetamidodiphenylamine gives p-nitroso-p'-acetamidodiphenylamine (54).



(27)

b. Base catalyzed migration. A 1,3-migration of the nitroso group from nitrogen to carbon appears to be required for an understanding of the base-catalyzed isomerization of certain N-nitrosohydrazones into corresponding oximes (55) (equation 28).



(28)

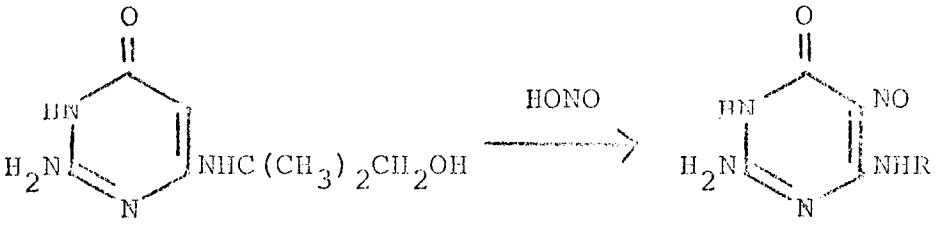
A base-catalyzed 1,2-migration of the nitroso group from nitrogen to carbon was recently discovered (56) (equation 29).

(29)

7. Nitrosation of primary aromatic amines

Under appropriate conditions a variety of primary aromatic amines will undergo nuclear nitrosation rather than diazotization. Nitrosyl sulfuric acid in concentrated sulfuric acid transforms

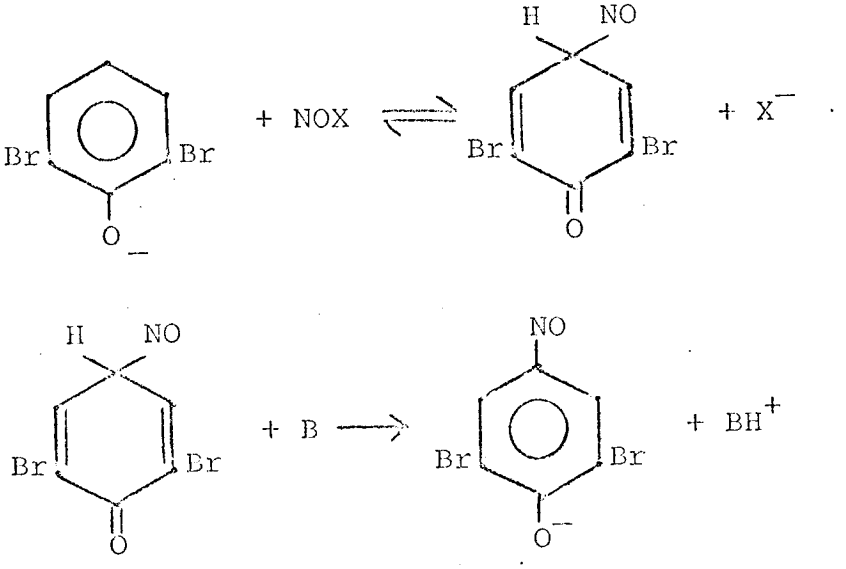
α-naphthylamine into its 4-nitroso derivative (57) and nitrous acid nitrosated a pyrimidine ring carbon in the presence of both a primary and secondary amine function (58) (equation 30). In a similar reaction nitrosation occurs at the 3-position in 2-hydroxy-4-amino-pyridine (59).



(30)

8. Nitrosation of phenols

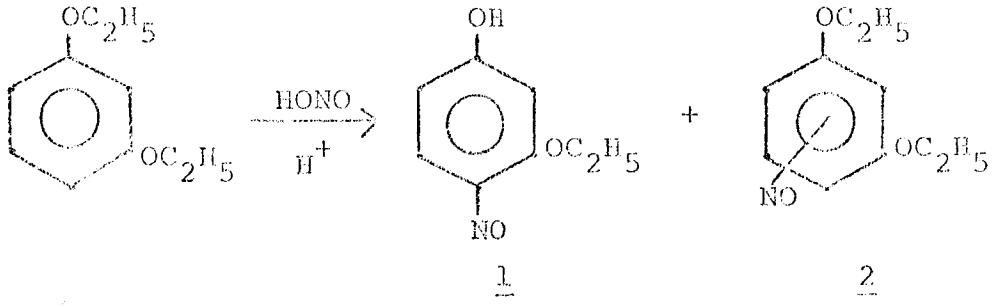
Phenols are readily nitrosated at o-and p-positions; thymol (60) and β-naphthol (60), undergo mononitrosation. Both 2,6-dibromophenol and 2,6-dibromophenol-4-D react with sodium nitrite in aqueous alcohol by general base catalysis (61) (equation 31) with nitrosodeprotonation occurring faster than nitrosodedeuteration ($k_H/k_D=3.6$). With nitrous acid, resorcinol is dinitrosated to 2,4-dinitrosoresorcinol (62) and phloroqucinol to trinitroso-phloroglucinol (62).



(31)

9. Nitrosation of aromatic ethers

Nitrosation of aromatic ethers is virtually unknown. In mineral acid containing an alkyl nitrite, resorcinol diethyl ether is partially transformed into a nitroso derivative of the diether (63) (equation 32). With the assumption that the unassigned nitroso group is at the 4-position in nitroso diethylresorcinol (2), the observed products are satisfactorily accounted for by the expected intermediates (equation 33).



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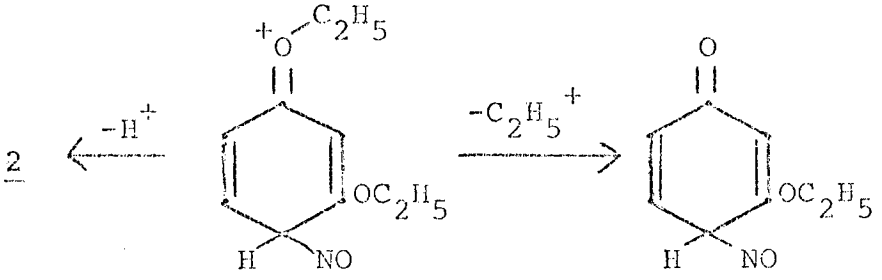
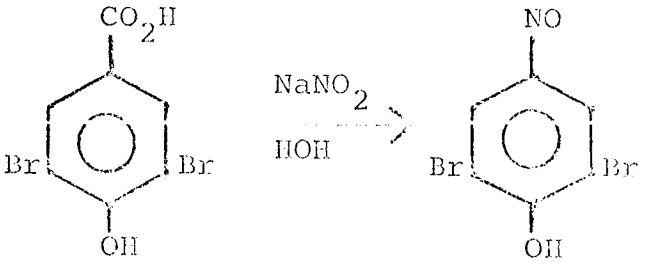


(33)

10. Nitrosative decarboxylation

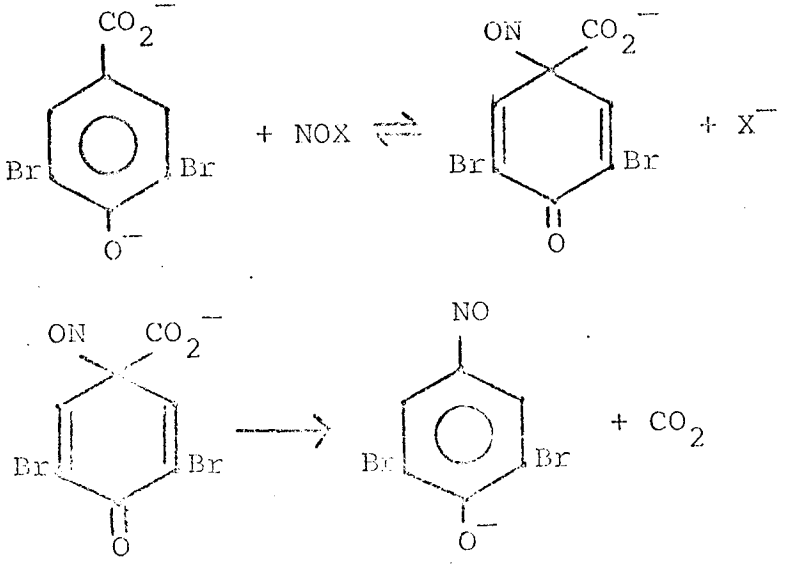
Nitrosation by displacement of substituents is rarely found. An interesting example has come to be known as nitroso

decarboxylation (64). On adding sodium nitrite to an aqueous alcoholic solution of 3,5-dibromo-4-hydroxybenzoic acid there is an immediate evolution of carbon dioxide. From the reaction, 3,5-dibromo-4-hydroxynitrosobenzene is isolated quantitatively (64) (equation 34).



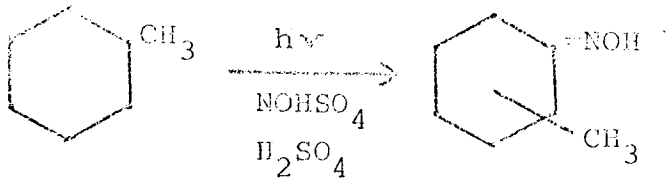
(34)

The kinetics of the reaction and comparison with bromodecarboxylation and bromodesulfonation are in agreement with the following mechanism (61) (equation 35). It is significant to note that p-hydroxybenzoic acid nitrosodecarboxylates at least 300 times more rapidly than does p-methoxybenzoic acid (61). Salicylic acid and its 3-,4- and 5-methyl derivatives undergo this reaction but 3- and 5-nitro and 3,5-dinitrosalicylic acid do not (64).

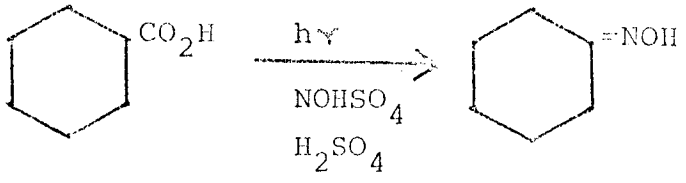


(35)

Following the observation that an attached methyl group decreased, whereas an attached carboxyl group increased, the reactivity of a tertiary carbon in a cyclohexane ring toward nitrosation by nitrosyl sulfuric acid in concentrated sulfuric acid (65) (equations 36, 37) it was found that cycloalkyl (ring-size 5 through 7) carboxylic acids and the α-branched carboxylic acids generally decarboxylated on similar treatment (66). The assumption that α-nitrosocarboxylic acids are intermediates (67) has been challenged and it is claimed that α-nitrosocyclohexane-carboxylic acid is not an intermediate in the nitrosative decarboxylation of cyclohexanecarboxylic acid with the formation of caprolactam (68).

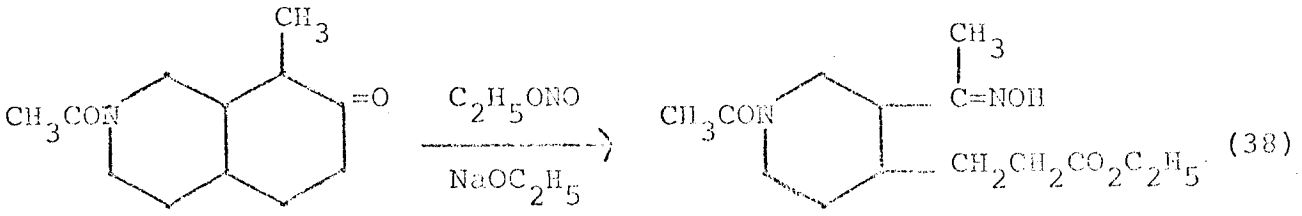


(36)



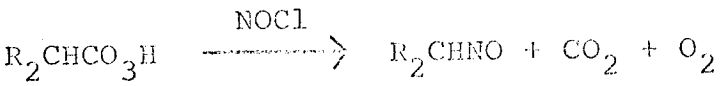
(37)

The carboxyl group may be replaced by other carbonyl groups, e.g., cyclododecanone oxime is obtained from formylcyclododecane (69) and cyclohexanone oxime is obtained from benzoylcyclohexane (70). These latter reactions are reminiscent of the base catalyzed nitrosation and cleavage of certain cyclic ketones (71) (equation 38).



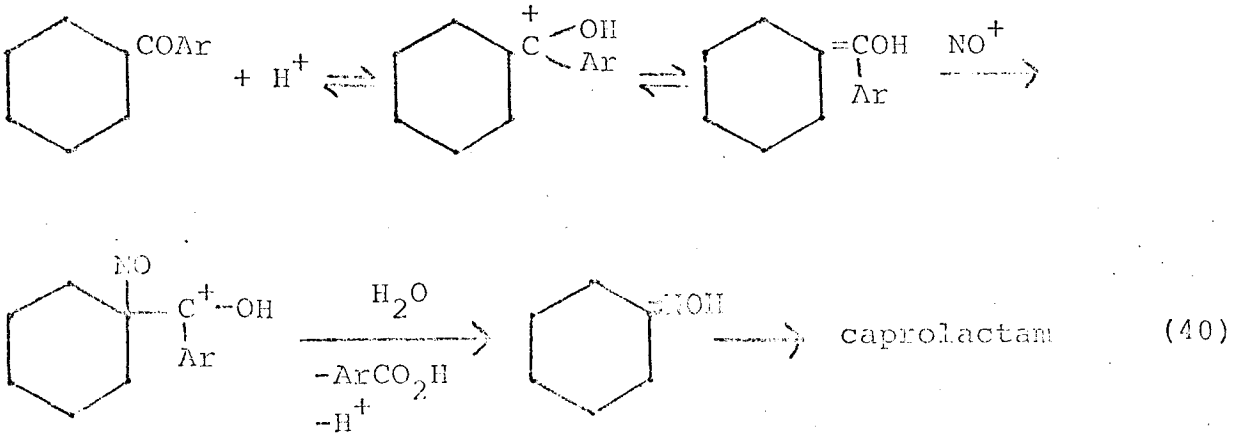
(38)

Another related reaction occurs when nitrosyl chloride transforms α-branched peroxycarboxylic acids into nitroso compounds (22) (equation 39).



(39)

Kinetic data for the reaction of aromatic ketones with nitrous acid in sulfuric acid is satisfied by a mechanism which involves the rate-determining step of deprotonation from the protonated ketone, followed by a rapid nitrosation and solvolysis (73) (equation 40) (cf. equation 62). This may be followed by tautomerization to an oxime and a Beckmann rearrangement. When the reaction is carried out with p-tolylcyclohexyl ketone and nitrosyl chloride in polyphosphoric acid, caprolactam and p-methylbenzoic acid are formed along with p-tolyl-α-nitrosocyclohexyl ketone (74).

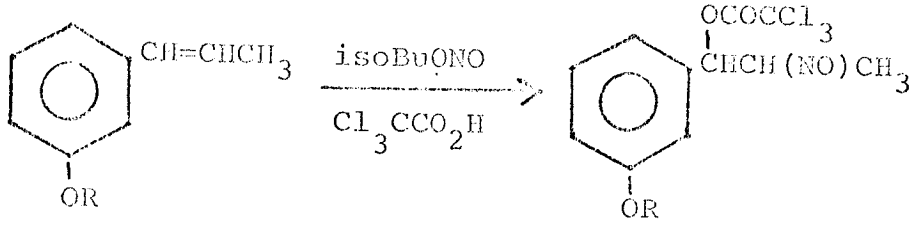


(40)

11. Nitrosation of olefins

a. Nitrous acid, nitrites, nitrogen oxides and nitrosoamines.

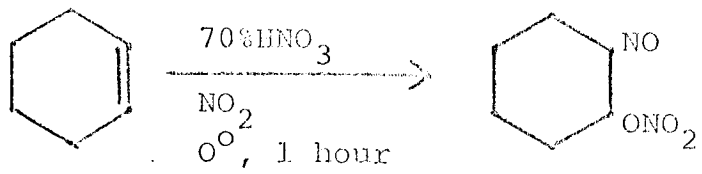
Other olefins may undergo nitrosation by a related mechanism, cf. equation 40. In trichloroacetic acid, certain ring-substituted derivatives of propenylbenzene treated with iso-butylnitrite are transformed into β-nitroso trichloroacetates (75) (equation 41). In contrast, the treatemnt of propenylbenzene with nitrous acid led to the formation of the corresponding nitrosite, 1-phenyl-1-nitroso-2-nitropropane (76) (equation 42) and similar results have been obtained with nitrogen trioxide (77). A β-nitroso nitrate has



(41)

$$C_6H_5CH{=}CHCH_3 \xrightarrow{HNO_2} C_6H_5\underset{NO}{\underset{|}{C}}HCH(NO_2)CH_3 \qquad (42)$$

been prepared from cyclohexene in concentrated nitric acid and nitrogen dioxide (equation 43) and a similar reaction has been reported for the initial product from isobutylene and dinitrogen tetroxide (equation 44) in the absence of weakly basic solvents such as ethers and esters which promote the formation of nitro compounds by a free radical process (78). A markedly different reaction transformed propylene into 2-nitro-3-methylfuroxan when treated with dinitrogen tetroxide (79) (equation 45).



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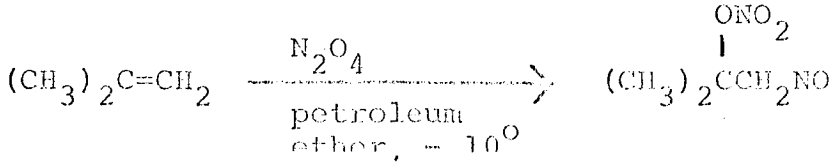
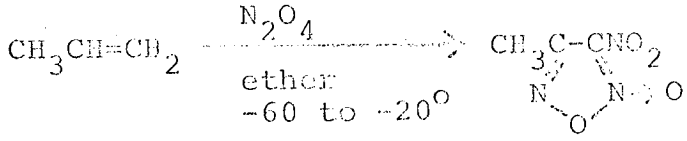


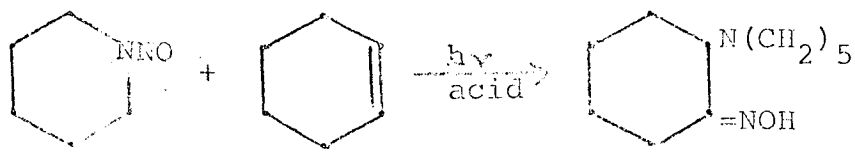
(44)



(45)

Nitrosites (ß-nitronitroso compounds, cf., equation 42) are generally produced from olefins treated with dinitrogen trioxide ($N_2O_3 \rightleftharpoons NO + NO_2$) (80). The reaction probably proceeds by a free radical mechanism initiated by an attack on an olefinic carbon by nitrogen dioxide, cf., equation 2. Terpene nitrosites are often solid derivatives helpful in characterization.

Photochemically produced adducts of nitrosamines and olefins have been reported. The adduct from N-nitrosopiperidine and cyclohexene has been isolated in its tautomeric oxime form (81) (equation 46).



(46)

b. Nitrosyl halides. Voluminous literature on the reaction of nitrosyl halides with a great variety of hydrocarbon and fluorocarbon olefins has recently appeared. The expected adduct (equation 47) is not only often formed along with other products but also it may occur as an intermediate required for the formation of a product isolated (82). Mono- and di-olefins

$$R_2C{=}CH_2 \xrightarrow{NOCl} R_2\underset{Cl}{C}CH_2NO \qquad (47)$$

(conjugated and unconjugated), ketene acetals, unsaturated alcohols, vinyl ethers, carbonyl compounds, nitroolefins and other hydrocarbon olefin derivatives will react with nitrosyl chloride generally under mild conditions. In certain instances, the nitroso halide may be produced *in situ* from an alkyl nitrite and hydrochloric or hydrobromic acid. Terpene nitrosochlorides have often been made for characterization purposes.

Fluorocarbon olefins also give adducts with nitrosyl halides (83) (equations 48, 49, 50).

$$CF_2{=}C(CF_3)_2 \xrightarrow[KF]{NOF} (CF_3)_3CNO \qquad (48)$$

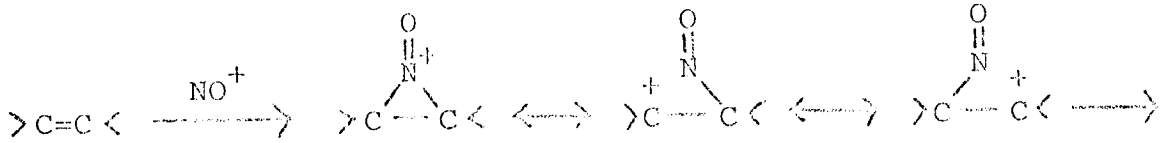
$$CF_3CF{=}CFOCH_3 \xrightarrow{NOCl} CF_3\underset{NO}{C}FCF(Cl)OCH_3 \qquad (49)$$

$$CF_2{=}\underset{CF_3}{C}COF \xrightarrow{NOF} (CF_3)_2C(NO)COF \qquad (50)$$

Both cis- and trans-nitrosohalide adducts of olefins may be formed (84). Solvent effects on the stereochemical course of the reaction has been demonstrated in the formation of the cis-adduct of cyclohexene in either chloroform, methylene chloride or trichloroethylene and the trans-adduct in liquid sulfur dioxide (85). A dependence on olefin structure has been observed in the formation of cis-adducts from nitrosyl chloride or bromide and norbornene in chloroform, and both anti-7-methoxynorbornene and norbornadiene in alcoholic acetic acid also containing hydrochloric acid (84). Each reaction occurred with no molecular rearrangement. Both a four-centered cyclic transition state leading exclusively to a cis-adduct and a three-membered nitrosonium intermediate which might give rise to either (or both) cis- and trans-adducts have been considered (84). An interconversion of initially formed cis-adducts between nitrosyl chloride and several olefins and the more stable trans-adduct (86) suggests that the addition reaction is reversible.

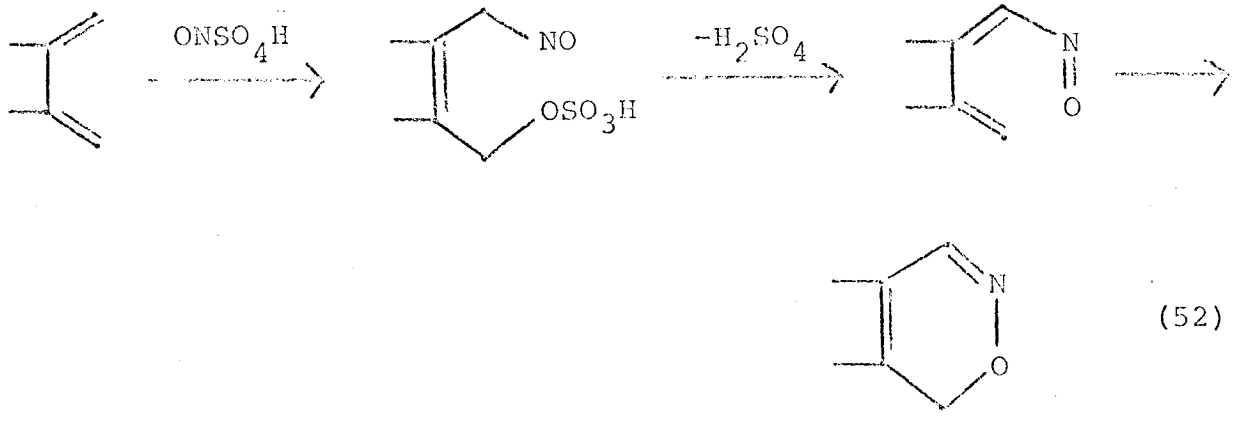
In a kinetic study of the addition of nitrosyl chloride to thirty different olefins in chloroform it was found that the reaction rate was influenced by both electronic and steric effects. Low activation enthalpies of 8.1 and 9.3 kcal/mol and activation entropies of -43.0 and -36.9 cal/mol.$^{-1}$ deg.$^{-1}$ were obtained for styrene and cyclohexene respectively. Rates for the addition to styrene and to cyclohexene increased in the solvent sequence: $CH_3OH < C_2H_5OH < CCl_4$, $C_6H_5CH_3 < n\text{-}C_7H_{16} < C_6H_5Cl < C_6H_4Cl_2$ $C_6H_5CN < CH_2Cl_2 < C_6H_5NO_2 < CHCl_3$ and addition of Lewis acids did

not accelerate the reaction (87). While the evidence seems to be accommodated by a cyclic onium intermediate (84) (equation 51) (cf., equation 40) a free-radical mechanism has not been eliminated (88); however, it would have to be initiated by a chlorine atom since it is well established that such a reaction could not be initiated by nitric oxide (see section B.1.).



products (51)

An unsaturated nitroso derivative of a bisulfate ester is formed on treatment of 2,3-dimethylbutadiene with nitrosylsulfuric acid. Apparently the reaction is one of conjugate addition since the ester readily cyclizes with the elimination of sulfuric acid and the formation of an oxazine (89) (equation 52). It seems probable that the loss of sulfuric acid occurs prior to ring-closure which then may occur by valence isomerization of a presumed nitrosobutadiene intermediate.



(52)

c. Dehydrohalogenation of olefin nitrosochlorides. In the presence of base the nitrosyl chloride adducts to olefins undergo dehydrochlorination to form α,β-unsaturated nitroso compounds. Styrene nitrosochloride with triethylamine in ether loses hydrogen chloride to form nitrosostyrene (90) (equation 53). In similar reactions nitrosoolefins have been formed from thujene nitrosochloride (91) and methyl oleate nitrosochloride (92).

$$C_6H_5\underset{Cl}{\underset{|}{C}}HCH_2NO \xrightarrow[\text{ether}]{Et_3N} C_6H_5CH{=}CHNO \qquad (53)$$

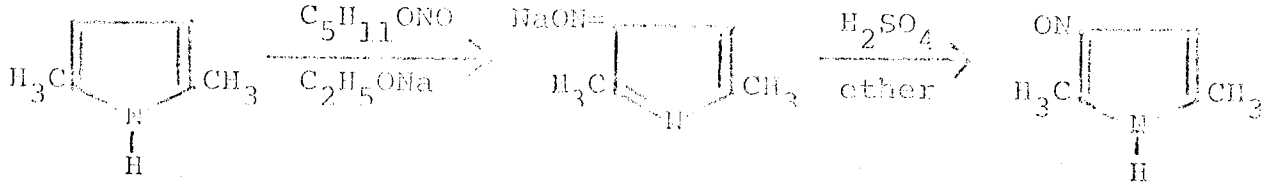
Dehydrobromination of the oxime of 3-bromo-3-methylbutanone-2 by alkali giving a polymer of 2-nitroso-3-methylbutene-2 has been claimed (93) (equation 54) but probably should be confirmed not only to clarify the structure of the polymer but also to elucidate the elimination mechanism insofar as initial isomerization to a nitroso compound is improbable. The reaction appears to give an example of the reversal of the conjugate addition to an α, β-unsaturated nitroso compound (cf. C. 2.).

$$(CH_3)_2\underset{Br}{\underset{|}{C}}\overset{NOH}{\overset{\|}{C}}-CH_3 \xrightarrow{KOH} (CH_3)_2C{=}\overset{NO}{\overset{|}{C}}CH_3 \longrightarrow \text{polymer} \qquad (54)$$

12. Nitrosation with nitrite esters and alkoxides

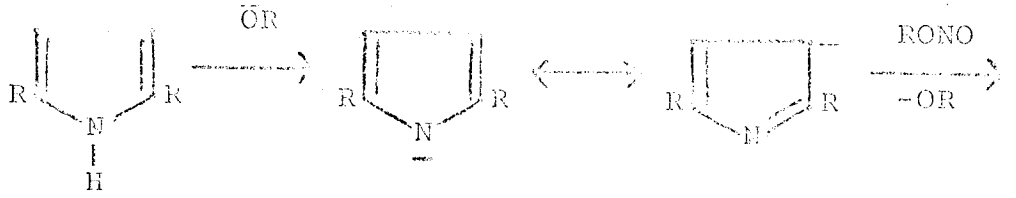
Certain phenols, e.g. resorcinol (94), and aromatic heterocycles may be nitrosated by an alkyl nitrite in the presence of

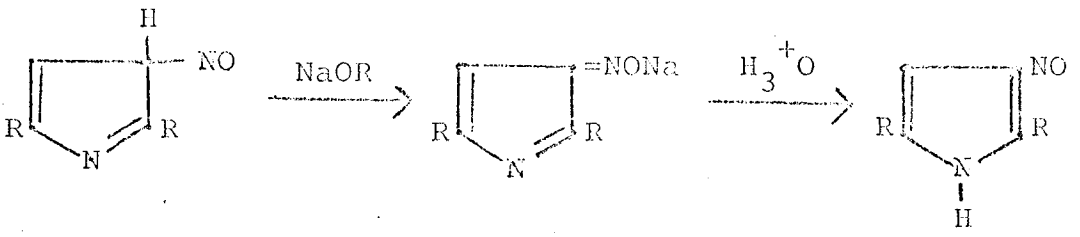
a metal alkoxide. From 2,5-dimethylpyrrole, treated in this manner a sodium salt may be obtained from which 3-nitroso-2,5-dimethylpyrrole may be liberated on mild treatment with acid (95) (equation 55). In a similar manner 3-nitrosoindoles



(55)

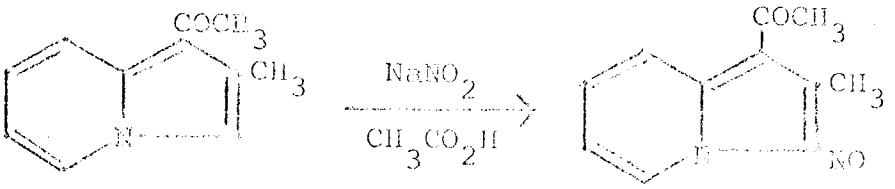
are obtained from the corresponding heterocycle and amyl nitrite (96). Apparently these are nitrosations of heterocycle anions (equation 56). When the heterocyclic nitrogen carries a substituent





(56)

in place of the acidic hydrogen, nitrosation may be achieved with nitrous acid (97, 98) (equations 57, 58).



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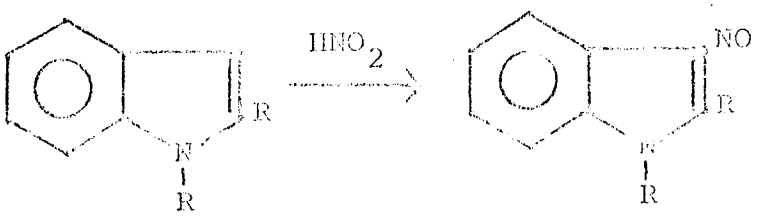
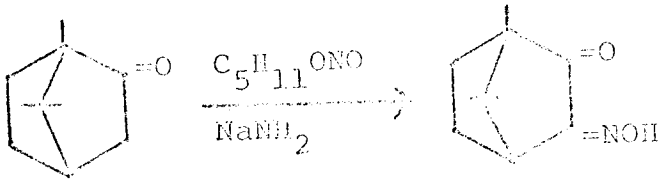


(58)

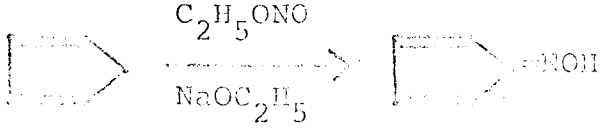
Imidazoles with a free 4-(or 5-) position and a ring nitrogen with an attached proton may be nitrosated by amyl nitrite and sodium ethoxide in a similar manner (99).

Both acid and base catalysis have provoked nitrosation at an aliphatic carbon atom with attached active hydrogen atom (100) (equations 59-63).



(59)

$$CH_3CH_2NO_2 \xrightarrow{HONO} CH_3C(=NOH)NO_2 \qquad (60)$$



(61)

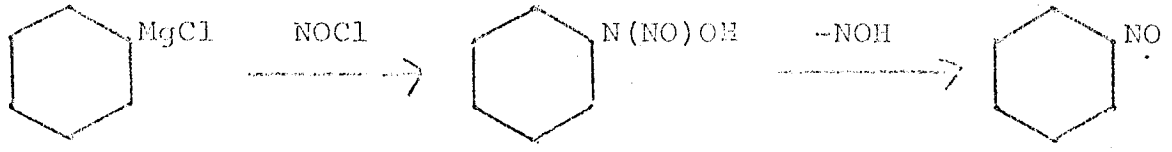
$$ArCOCH_2Cl \xrightarrow[HCl]{C_4H_9ONO} ArCOCCl \underset{NOH}{\parallel} \qquad (62)$$

$$RCH(CO_2H)_2 \xrightarrow[HCl]{R'ONO} RCCO_2H \underset{NOH}{\parallel} \qquad (63)$$

Presumably the reaction, whether acid or base catalysed, proceeds by electrophilic attack on an α-carbon atom in agreement with other condensation reactions of active methyl, methylene and methynyl groups.

13. Organometallic compounds and nitrosyl chloride

Alkylnitrosohydroxylamines (101) are often products from reactions between alkylmetals and nitrosyl chloride (equation 64). Nitrosohydroxylamines may lose nitrosylhydride with the formation of the corresponding nitroso compound (101). Nitrosobenzene has

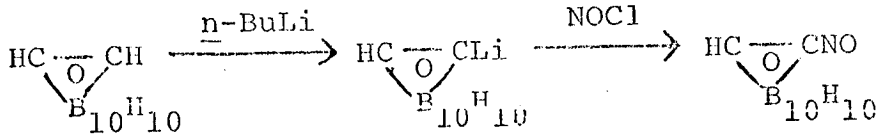


(64)

been prepared by passing nitrosyl chloride into a solution of phenylmagnesium bromide (102) and pentamethylnitrosobenzene from the corresponding arylmercuriacetate and ethyl nitrite in hydrochloric acid (103).

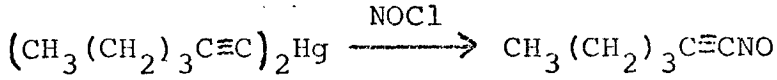
Recently a nitrosocarborane has resulted from the treatment of 1-carboranyl-lithium with nitrosyl chloride (104) (equation 65) and nitrosoalkane dimers result from the similar treatment of an

aluminum trialkyl with nitrosyl chloride (105). Tricyclohexylboron and nitrosyl sulfuric acid reacted with the apparent initial formation of nitrosocyclohexane; however, products isolated represented further changes (106).



(65)

The long unknown 1-nitrosoacetylenes were first produced in a reaction in which nitrosyl chloride attacked an organomercury bond (107) (equation 66).



(66)

14. Geminal nitrosohalides from oximes

Oximes are transformed into gem-halonitroso derivatives on treatment with hypohalous acid. Development of the blue color of the product is the basis for Piloty's qualitative determination of the presence of an oxime (108). With only occasional bursts of interest, Piloty's reaction lay dormant until gem-chloronitroso derivatives of hydrocarbons attracted attention as products in the reaction between irradiated nitrosyl chloride and hydrocarbons or irradiated mixtures of chlorine, nitric oxide

and hydrocarbons (109). The principal product is an oxime as is demonstrated in this important method for the synthesis of cyclohexanone oxime, an intermediate in a preparation of caprolactam.

Oxidation of the product to the corresponding halonitro derivative by halogens in an alkaline medium may be eliminated by treating the oxime with chlorine in ether (110) or by treatment with chloroamides, e.g. N-chloroacetamide, N-chlorocaprolactam, N-chlorourea and N,N-dichlorosulfonamides (111). N-Bromosuccinimide in aqueous sodium carbonate has also been used (112). A lesser known reaction discovered by Rheinboldt (113) occurs between nitrosyl chloride and an oxime (equation 67) and is especially interesting in its application to aldoximes.

$$R_2C{=}NOH \xrightarrow[-NO\ -HCl]{NOCl} R_2C(NO)Cl \qquad (67)$$

Explanations for the transformation of ketoximes into gem-halonitrosoalkanes on treatment with halogen have been based upon conceivable tautomers for an oxime. Halogenation of a tautomeric monofunctional primary or secondary nitrosoalkane appears to be unlikely since their prototropic rearrangement in the gas phase, melt or in solution into oximes is not detectably reversible (114) (equation 68). In addition, it is reported that nitrosoparaffins

are not halogenated under the conditions which transform oximes into gem-halonitrosoalkanes (115). Addition of chlorine to the

$$R_2CHNO \longrightarrow R_2C{=}NOH \qquad (68)$$

oxime double bond followed by an elimination of hydrogen chloride (equation 69) has been accepted as more probable (110) but has been challenged (115) on the basis of an apparent requirement for hydrogen to be attached to at least one α-carbon

$$R_2C{=}NOH \xrightarrow{Cl_2} R_2\overset{Cl}{\underset{|}{C}}-\overset{Cl}{\underset{|}{N}}-OH \xrightarrow{-HCl} R_2C(Cl)NO \qquad (69)$$

in the oxime. Of twelve monoximes which lacked hydrogen at an α-carbon, only Michler's ketone oxime reacted, as predicted, in the presence of acid, with chlorine with the formation of a nitroso compound. Although the proposed requirement for hydrogen attached to at least one α-carbon was fulfilled in 75 examples of oximes which were transformed by chlorine into nitroso derivatives, it is difficult to understand why o- and m-nitroacetophenone oximes each failed to react whereas acetophenone and p-nitroacetophenone oximes did. Other reactions between chlorine and oximes which also contain additional reactive functional groups may occur. Benzoin oxime, for example, was not transformed into a nitroso derivative and was apparently oxidized to benzil.

monoxime. Nitroso compounds were not obtained from α-dioximes but these are known to be transformed into furoxans under the conditions employed (116).

To account for the possibility of participation by hydrogen at an α-carbon, Kosinski has proposed (115) a mechanism which invokes Raikova's tautomerization of an oxime (117) (equation 70). Following chlorination at nitrogen in a vinyl

$$RCH_2\underset{\underset{NOH}{\|}}{CR^1} \rightleftharpoons RCH{=}\underset{\underset{NHOH}{|}}{CR^1} \rightleftharpoons RCH_2\underset{\underset{HON}{\|}}{CR^1} \qquad (70)$$

hydroxylamine, this mechanism requires elimination of, followed by recombination with, hydrogen chloride (115) (equation 71); however, the final step in equation 71 must be questioned insofar as conjugate addition of hydrogen chloride to an α,β-unsaturated nitrosoalkene would be expected (equation 72), cf. C.22.

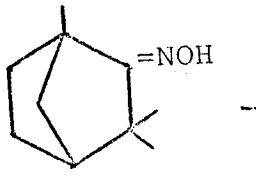
$$RCH{=}\underset{\underset{NHOH}{|}}{CR^1} \xrightarrow[-HCl]{Cl_2} RCH{=}\underset{\underset{OH}{|}}{\overset{\overset{NCl}{|}}{CR^1}} \longrightarrow RCH{=}\underset{\underset{HCl\cdot NO}{|}}{CR^1} \longrightarrow RCH_2\overset{\overset{Cl}{|}}{\underset{\underset{NO}{|}}{CR^1}} \qquad (71)$$

$$RCH{=}\underset{\underset{R^1}{|}}{CNO} \xrightarrow{HCl} RCH(Cl)-C(R^1){=}NOH \qquad (72)$$

After the report that hexafluoroacetoxime reacts with chlorine at -78° and is transformed into the corresponding gem-nitrosochloride (118) (equation 73), the proposed requirement for participation by hydrogen attached to an α-carbon must be reevaluated. Benzophenone oxime in the presence of chlorine underwent a Beckmann rearrangement into benzanilide (115).

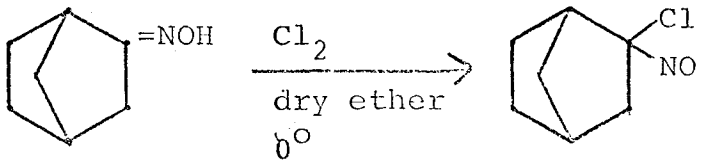
$$(CF_3)_2C{=}NOH \xrightarrow[-78^{\circ}]{Cl_2} (CF_3)_2C(NO)Cl \qquad (73)$$

An example of an aliphatic ketoxime which does not contain hydrogen on an α-carbon is found in fenchone oxime, which is unreactive toward chlorine bubbling through alkaline or neutral solutions of the oxime (115) (equation 74). In contrast norcamphor



$$\xrightarrow{Cl_2} \text{No reaction} \qquad (74)$$

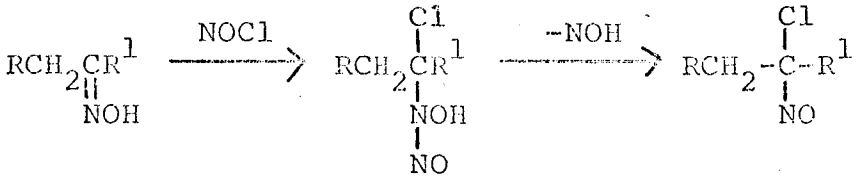
oxime is transformed into the gem-halonitrosoderivative (119) (equation 75).



(75)

The reaction between nitrosyl chloride and oximes may also give gem-nitrosochlorides. Addition of nitrosyl chloride to the

oxime linkage followed by elimination of nitrosyl hydride has been suggested (120) (equation 76). In support of the final step it is known that N-nitrosohydroxylamines reversibly



(76)

dissociate into C-nitroso derivatives and nitrosyl hydride (101, 121). Oximes which are ordinarily unreactive to nitrosyl chloride include the oximes of benzophenone, fluorenone, phenanthrenequinone and other ketones some of which contain hydrogen at an α-carbon (113).

15. Esters of geminal nitrosoalcohols from oximes

Two methods for oxidation at the α-carbon of nitroso compounds are reminiscent of the reactions leading to the formation of gem-nitrosohaloalkanes discussed in the last section.

The intermediacy of a gem-nitrosofluoro derivative was assumed in the formation of dimethyl flucronitromalonate from the reaction between potassium dimethyl oximinomalonate and perchloryl fluoride in dimethylformamide (122) (equation 77) and in the same reaction mixture the formation of a perchlorate ester of a gem-hydroxynitroso derivative is considered in an explanation for the formation of another product, a ketomalonic ester.

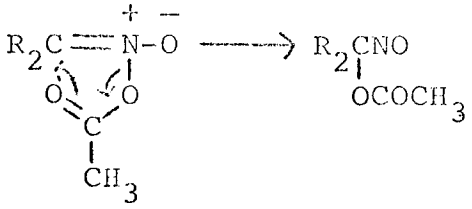
$$(CH_3O_2C)_2C{=}NO^- \xrightarrow{FClO_3} (CH_3)_2C)_2C{=}NOClO_3 \longrightarrow$$

$$(CH_3O_2C)_2\overset{\overset{NO}{|}}{C}OClO_2 \longrightarrow (CH_3O_2C)_2CO + \bar{N}O_3 + \bar{C}l$$

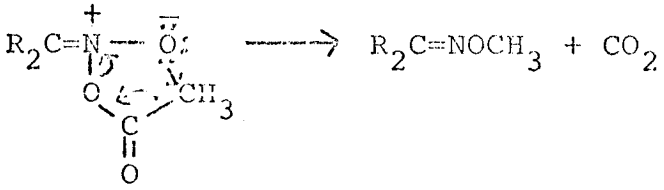
$$(CH_3O_2C)_2C{=}NOClO_3 \xrightarrow[(\bar{C}l \text{ or } F^-)]{X^-} (CH_3O_2C)_2C(NO)X \xrightarrow{[O]} \qquad (77)$$

$$(CH_3O_2C)_2C(NO_2)X$$

In the other oxidation, gem-nitrosoacetates are produced from ketoximes and lead tetraacetate (123) (equation 78) and oxime O-methyl ethers are reported as by-products (125). Nitrosobenzoates are similarly prepared with lead tetrabenzoate (124). The suggestion (123, 125) that the reaction proceeds with the intermediate formation of free radicals has been confirmed by an e.s.r. study of comparatively stable iminoxy radicals obtained from ketoximes by oxidation with lead tetraacetate. It was concluded that the unpaired spin density resided on oxygen and nitrogen and that the structure was best described as a resonance hybrid: $R_2C{=}\ddot{N}{-}\ddot{\underset{\cdot\cdot}{O}}\cdot \longleftrightarrow R_2C{=}\dot{N}{-}\ddot{\underset{\cdot\cdot}{O}}:$ (126). This result is consistent with initial acetoxylation at nitrogen from which either a gem-nitrosoacetate or an oxime O-methyl ether could be formed (equations 78 and 79). Further interaction between the gem-nitrosoacetate and acetoxy radicals may occur (126).



(78)

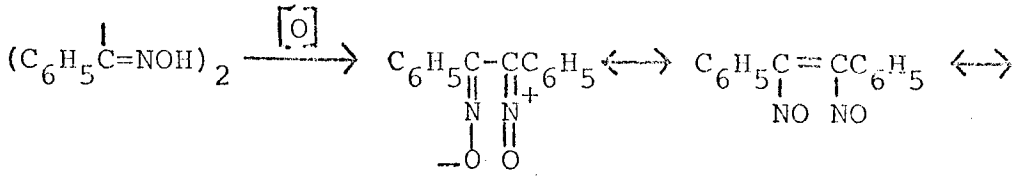


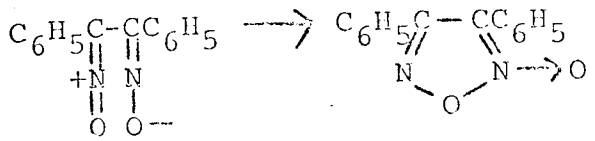
(79)

For a discussion of α-hydroxynitroso compounds in the Nef reaction see B.23.

16. Oxidation of dioximes

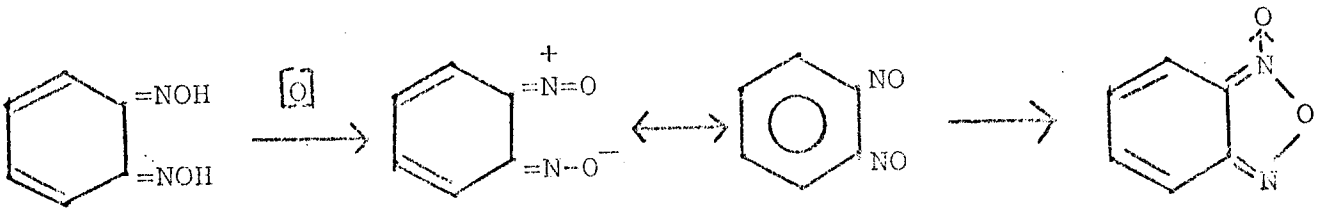
Oxidation of dioximes of α-diketones may lead to the formation of furoxans (116). Benzil dioxime when treated with alkaline ferricyanide, chlorine in ethanol or benzene, alkaline hypochlorite, or dinitrogen trioxide is transformed into diphenylfuroxan (equation 80).



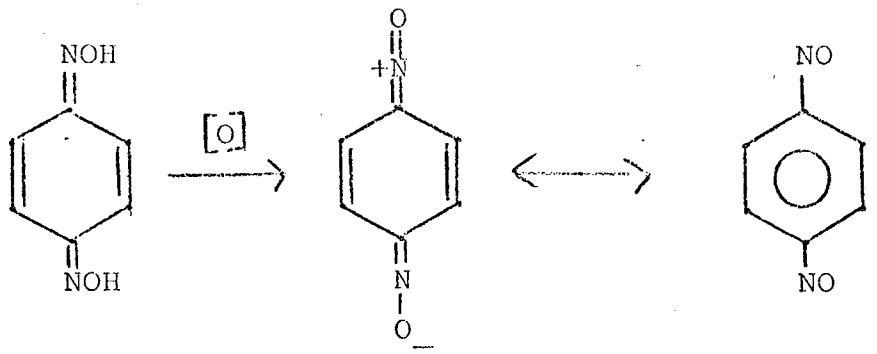


(80)

The intermediacy of 1,2-diphenyl-1,2-dinitrosoethylene is assumed; however, it appears likely that the zwitterionic form of the intermediate is the important species leading to ring-closure. Both furoxans are generally obtained from glyoximes in which the two substituents at carbon are different. The dioximes of both o- and p- benzoquinone undergo similar oxidations (116) (equation 81). An interesting analogy for



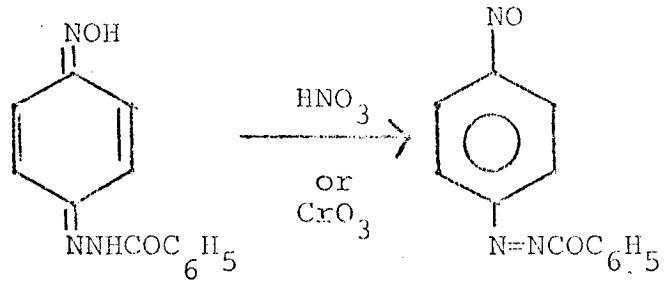
2 structures



(81)

2 structures

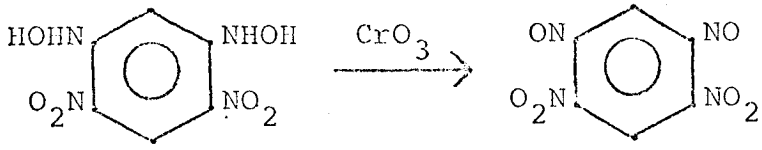
the latter reaction is found in the oxidation of an oxime hydrazone derivative of p-benzoquinone (127) (equation 82).



(82)

17. Oxidation of hydroxylamines

Oxidation of hydroxylamines is a preferred method for the preparation of corresponding nitroso derivatives but limited in application by the accessibility of the starting materials which generally are reduction products from nitro compounds or oxidation products from primary amines. In such a two-step process nitrobenzene is reduced by zinc and ammonium chloride to phenylhydroxylamine which is oxidized by sodium dichromate in sulfuric acid to nitrosobenzene in overall yield of nearly 55% (128). Other reagents which have been used to oxidize hydroxylamines include mercuric oxide (129), potassium ferricyanide (130) periodates in alkaline medium (131) periodic acid (132) chlorine (133), air (134) and chromium trioxide (135, 136) (equations 83, 84, 85, 86).



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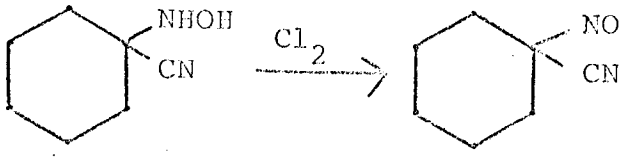
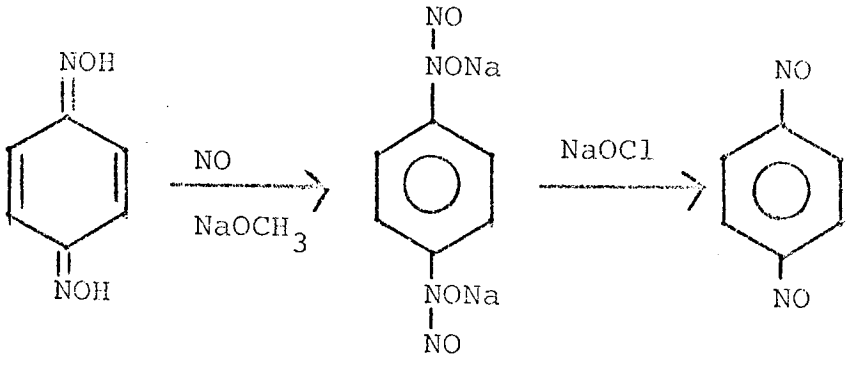


(84)

$$HC(=NOH)NHOH \xrightarrow[\text{alkali}]{KIO_4} HC(=NOK)NO \qquad (85)$$

$$(F_3C)_2C{=}NOH \xrightarrow[CrO_3]{HF} (F_3C)_2C(F)NO \qquad (86)$$

Although N-nitrosohydroxylamines tend to dissociate into nitroso derivatives and nitrosyl hydride (101), the presence of sodium hypochlorite is advantageous (137) (equation 87).



(87)

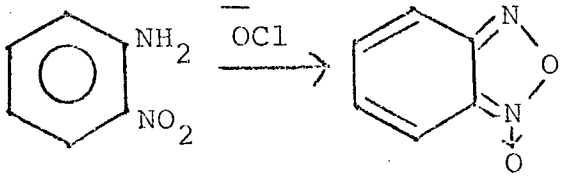
Hydroxylamines have a tendency to disproportionate into the corresponding nitroso compound and amine. After three weeks in a closed vessel, pure mesitylhydroxylamine had changed into 2,4,6-

trimethylnitrosobenzene and mesidine, along with 2,4,6-trimethylnitrobenzene and azomesitylene (138).

18. Oxidation of primary amines

Oxidation of primary amines to hydroxylamines requires a reagent which attaches oxygen to nitrogen. Reagents which have been successful include Caro's acid (monoperoxysulfuric acid), peroxyacetic and certain other organic peroxy acids or peroxy anhydrides, hydrogen peroxide in acetic acid, permanganate (often with formaldehyde) and hypochlorous acid. Generally the subsequent oxidation occurs readily thereby providing an important route for the preparation of nitroso compounds. The elimination or suppression of further oxidation, e.g., oxidation at nitrogen to the corresponding nitro compound or oxidation at carbon, is often a limiting factor to consider.

Nitrosobenzene is one of at least seven oxidation products obtained when aniline is treated with hypochlorous acid (139). On the other hand, the oxidation of o-nitroaniline by a hypochlorite solution is a preferred method for the preparation of benzfuroxan (116) (equation 88). An improved yield of



(88)

nitrosobenzene is reported for the oxidation of aniline by permanganate with formaldehyde in sulfuric acid (140), a method which transforms cyclohexylamine into nitrosocyclohexane in yields over 80% (141). The latter oxidation is also effected by hydrogen peroxide in the presence of sodium tungstate (142).

Bamberger found Caro's acid to be a general reagent for oxidizing aliphatic primary amines in which the amino group is attached to a tertiary carbon atom and for primary aromatic amines (143, 144). Quantitative amounts of nitroso compounds were obtained from the isomeric nitroanilines (145). Apparently, the oxidation is facilitated by electron releasing groups; p-phenylenediamine is transformed into p-nitroaniline, but p-nitrosoaniline may also be isolated when the reaction is carried out in ether (146) (equation 88a). Acylation of one amino group

$$p\text{-}C_6H_4(NH_2)_2 \xrightarrow[\text{ether}]{H_2SO_5} p\text{-}H_2NC_6H_4NO + p\text{-}H_2NC_6H_4NO_2 \qquad (88a)$$

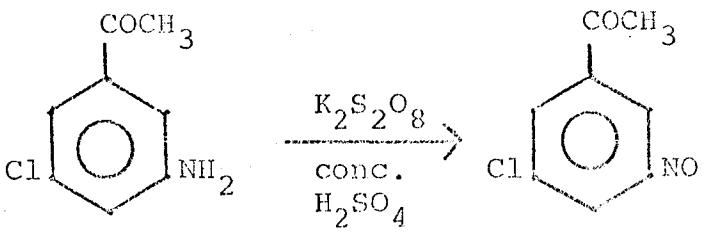
controls the oxidation which proceeds to the formation of a nitroso derivative without substantial further oxidation (147).

After three minutes Caro's acid in ether can oxidize tert-butylamine to 2-methyl-2-nitrosopropane (144). Better yields are obtained in the similar oxidation of 4-amino-4-methylpentanone-2 (144) (equation 89). The intermediate formation of nitroso

compounds in the oxidation of tertiary alkyl primary amines to corresponding nitroparaffins is demonstrated by the formation of a characteristic blue color which persists if oxidation is incomplete (148).

$$H_2NC(CH_3)_2CH_2COCH_3 \xrightarrow{H_2SO_5} ONC(CH_3)_2CH_2COCH_3 \qquad (89)$$

Good yields have been reported for the oxidation of primary aromatic amines to corresponding nitroso derivatives by a peroxydisulfate in concentrated sulfuric acid (149) (equation 90) but



(90)

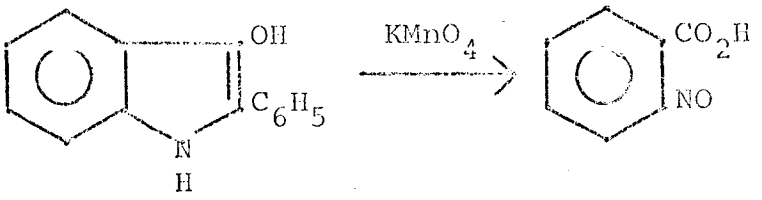
perphosphoric acids failed to transform certain primary aromatic amines into nitroso compounds (150).

Nitrosobenzene along with phenol, diphenylamine, ammonia and nitrobenzene was a detected product following x-ray irradiation of an aqueous solution of aniline (151).

19. Oxidation of secondary amines.

There are a few reports of the formation of nitroso compounds from the oxidation of secondary amines. By Caro's acid, N-benzylaniline is transformed into nitrosobenzene, nitrobenzene,

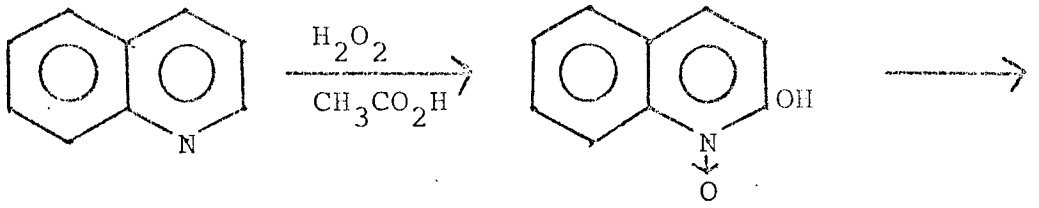
azoxybenzene and benzoic acid (149). Nitrosobenzene is one of at least eight products obtained from N-methylaniline on treatment with Caro's acid (152). Cold dilute permanganate solutions transform 2-phenyl-3-hydroxyindole into o-nitrosobenzoic acid (153) (equation 91).

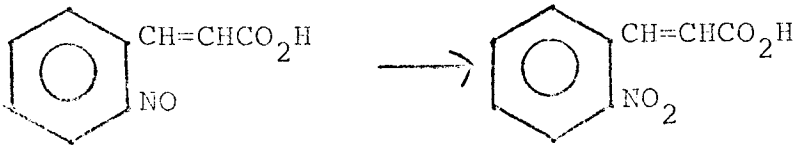


(91)

20. Oxidation of tertiary amines

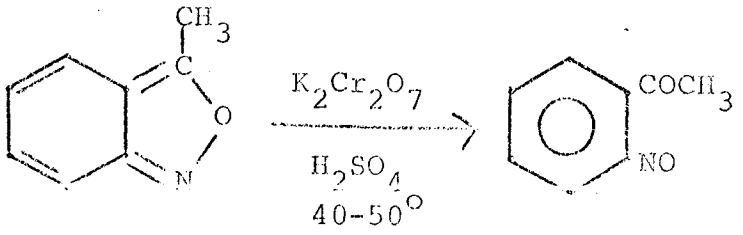
o-Nitrosocinnamic acid is a proposed intermediate in the oxidation of quinoline by hydrogen peroxide in acetic acid to o-nitrocinnamic acid (154) (equation 92).





(92)

It is reported that oxidation of 3-methylanthranil occurs with opening of the isoxazole ring and the formation of o-nitroso-acetophenone (155) (equation 93).



(93)

21. Oxidation of nitrones and Schiff bases

Ozonization of nitrones has produced nitroso compounds (156) (equation 94). Similar treatment of Schiff bases did not give nitroso products (156); however the presence of a blue color during the ozonization of the Schiff base derived from tert-butyl amine and isobutyraldehyde has been offered as evidence for the formation of 2-nitroso-2-methylpropane (157) (equation 95). It was carefully established that the oxidant was ozone rather than oxygen somewhat in contrast with the catalytic oxidation of certain perfluoro Schiff bases (158) (equation 96) in which trifluoronitrosomethane was a considered intermediate.

$$C_6H_5\overset{\overset{O}{\uparrow}}{C}H{=}NR \xrightarrow{O_3} C_6H_5CHO + RNO$$

$$R{=}C_6H_5, \text{t-}C_4H_9 \qquad (94)$$

$$(CH_3)_3CN{=}CHCH(CH_3)_2 \xrightarrow{O_3} (CH_3)_3CN\overset{O}{\diagdown\diagup}CHCH(CH_3)_2 + (CH_3)_3CNO \quad (95)$$

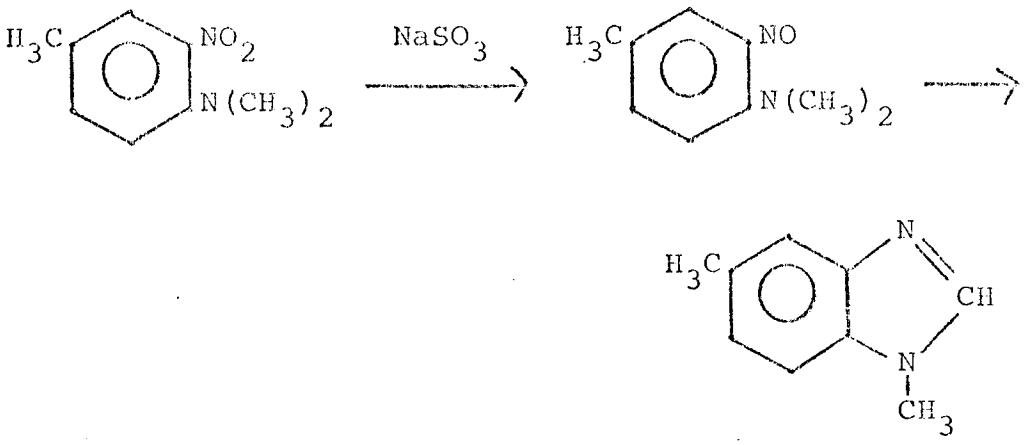
$$CF_3N{=}CF_2 + O_2 \xrightarrow[400^{o}]{RbF} 2COF_2 + NOF$$

$$CF_3N{=}CF_2 + NOF \longrightarrow (CF_3)_2N{-}NO \quad (96)$$

22. Reduction and deoxygenation of nitro compounds

Reduction of a nitro compound leads first to the formation of a nitroso compound. In an acid medium the latter is rapidly reduced to an amine with the corresponding hydroxylamine as an intermediate. Reduction in an alkaline medium gives rise to an azoxy compound resulting from a condensation between the nitroso compound and the corresponding hydroxylamine. Best yields of nitroso compounds are generally obtained from reductions in neutral media. The exceptional reduction of primary and secondary nitroparaffins by stannous chloride does not proceed beyond the initial stage presumably because rapid isomerization to an oxime takes place.

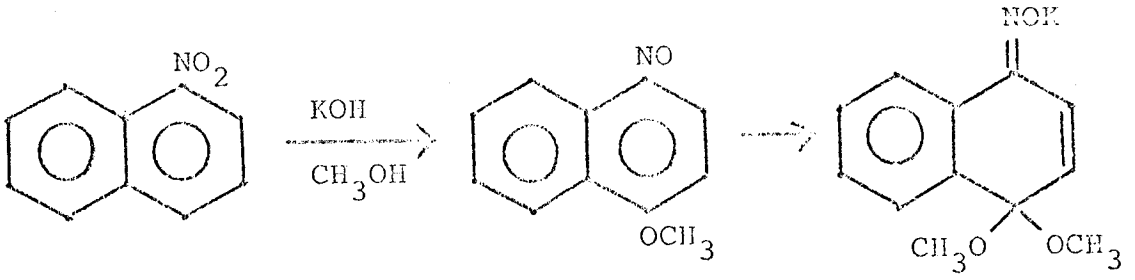
An electrolytic reduction of nitrobenzene with a neutral electrolyte gave a good yield of nitrosobenzene (159). Poor yields have been reported for deoxygenation with barium oxide (160) and reduction with hydroxylamine in methanol (161) or metallic salts such as mercuric chloride, zinc chloride (162) or sodium bisulfite (163). In the latter example nitroso compounds are intermediates in the reductive sulfonation of aromatic nitro compounds to aminosulfonic acids (Piria reaction). With an intramolecular condensation the reduction of 3-nitro-4-dimethylaminotoluene was stopped at the nitroso stage with the formation of 1,5-dimethylbenzimidazole (163) (equation 97).



(97)

m-Trifluoromethylnitrobenzene is reduced to the corresponding nitroso compound by ethyl mercaptan (165). Aromatic o- and p-nitronitroso derivatives are produced by treating the corresponding dinitro compounds with either hydroxylamine or stannous

oxide in methyl alcoholic alkali (166). The behavior of α-nitronaphthalene towards alcoholic alkali is especially interesting. First one and eventually two methoxy groups become attached to the C4 position (167) (equation 98). Presumably a related process is required in the formation of p-nitrosodiphenylamine from aniline and nitrobenzene in alkali (168) (equation 99).



(98)

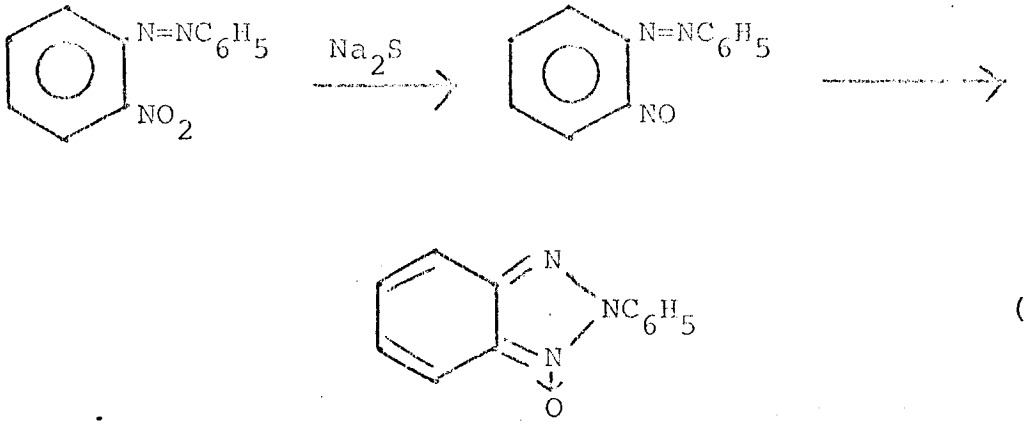
$$C_6H_5NH_2 + C_6H_5NO_2 \xrightarrow[125^{\circ}]{\text{alkali}} p\text{-}C_6H_5NHC_6H_4NO \qquad (99)$$

A deoxygenation mechanism probably best accounts for the formation of nitrosobenzene from nitrobenzene treated with iron powder in the presence of carbon dioxide at 220° (169). Similar deoxygenations have been carried out in dry organic solvents with sodium, potassium, calcium, strontium, barium, magnesium, zinc and aluminum amalgam (170). Deoxygenation of aromatic nitro derivatives by free radicals also leads to the formation of corresponding nitroso compounds (171). Dimeric nitrosobenzene

iron tricarbonyl is produced on irradiation of iron pentacarbonyl in nitrobenzene (172) (equation 100).

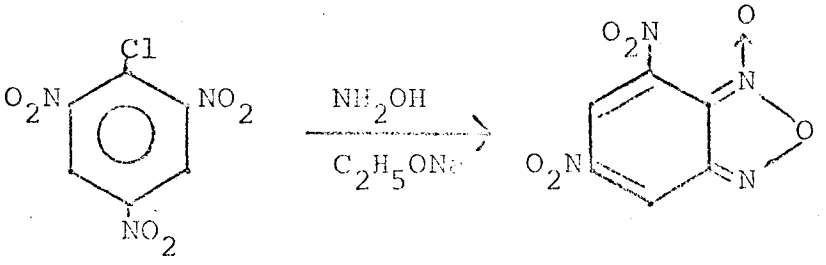
$$Fe(CO)_5 + C_6H_5NO_2 \xrightarrow[HCl]{h\nu} \left[C_6H_5NOFe(CO)_3\right]_2 \qquad (100)$$

Ring-closure of an intermediate o-nitrosoazobenzene presumably accounts for the absence of further reduction of o-nitroazobenzene by sodium sulfide (173) (equation 101). A similar reason



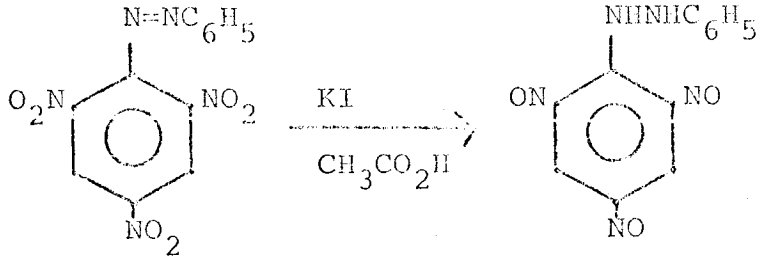
(101)

may be applied to (but is not necessarily required for) the deoxygenation of a nitro group in the transformation of picryl chloride into 4,6-dinitrobenzfuroxan by hydroxylamine in the presence of sodium ethoxide (174) (equation 102).



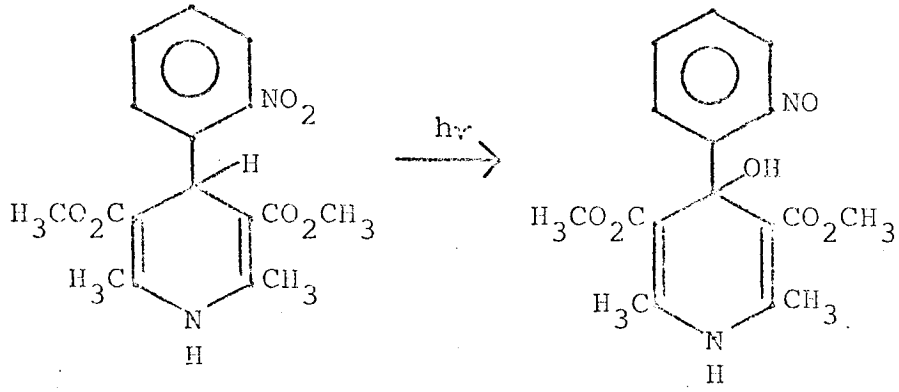
(102)

In view of the paucity of information on aromatic m-dinitrosoderivatives the reported formation of N-1,3,5-trinitrosophenyl-N'-phenylhydrazine from picrylazobenzene treated with potassium iodide in acetic acid takes on added interest (175) (equation 103).



(103)

By intramolecular transfer of oxygen certain nitro groups are readily deoxygenated. A classic example is found in the photochemical isomerization of o-nitrobenzaldehyde into o-nitrosobenzoic acid (176) which takes place both in solution and in the solid state. m- and p-Nitrobenzaldehydes do not give nitroso compounds, but certain other o-nitro derivatives undergo similar rearrangements (equations 104, 105, 106).



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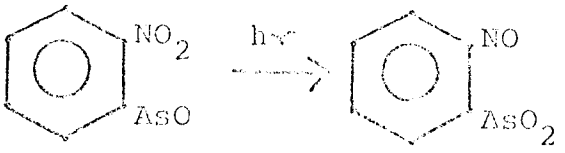

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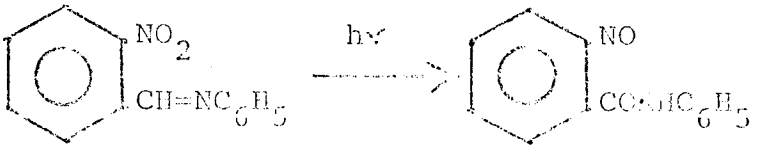
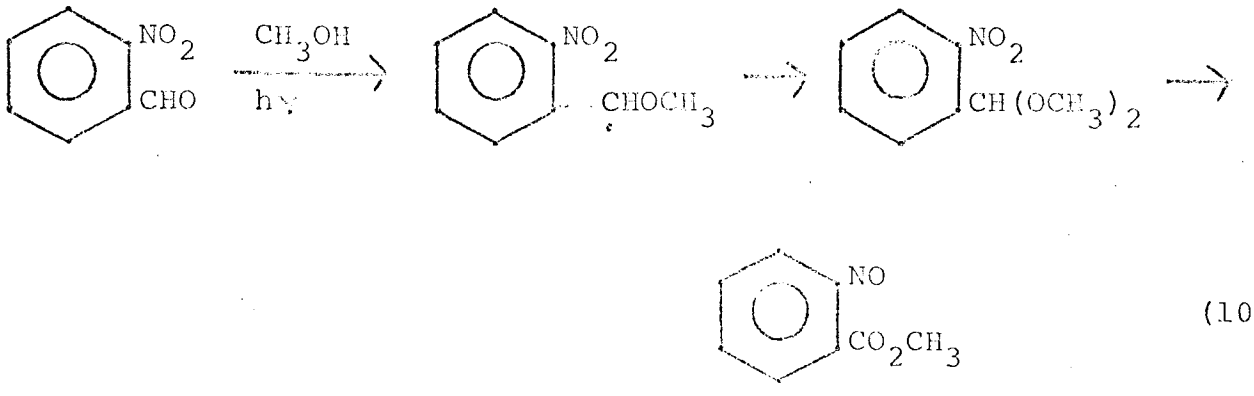


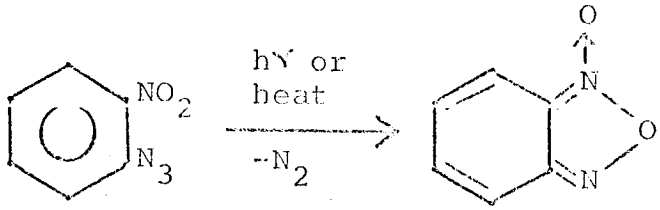
(106)

In the isomerization of o-nitrobenzaldehyde, the transfer of oxygen from an activated nitro group to the carbonyl carbon probably occurs by a redistribution of electrons when the nitro and aldehyde groups are coplanar with the aromatic ring (180). A kinetic study by e.s.r. of free radicals produced during the reaction did not lead to a definitive explanation (181). When the reaction is run in methanol, it is claimed that irradiation first brings about the formation of the dimethylacetal of o-nitrobenzaldehyde from an intermediate methoxy-o-nitrobenzyl radical (182) (equation 107). The acetal is then transformed into methyl o-nitrosobenzoat .



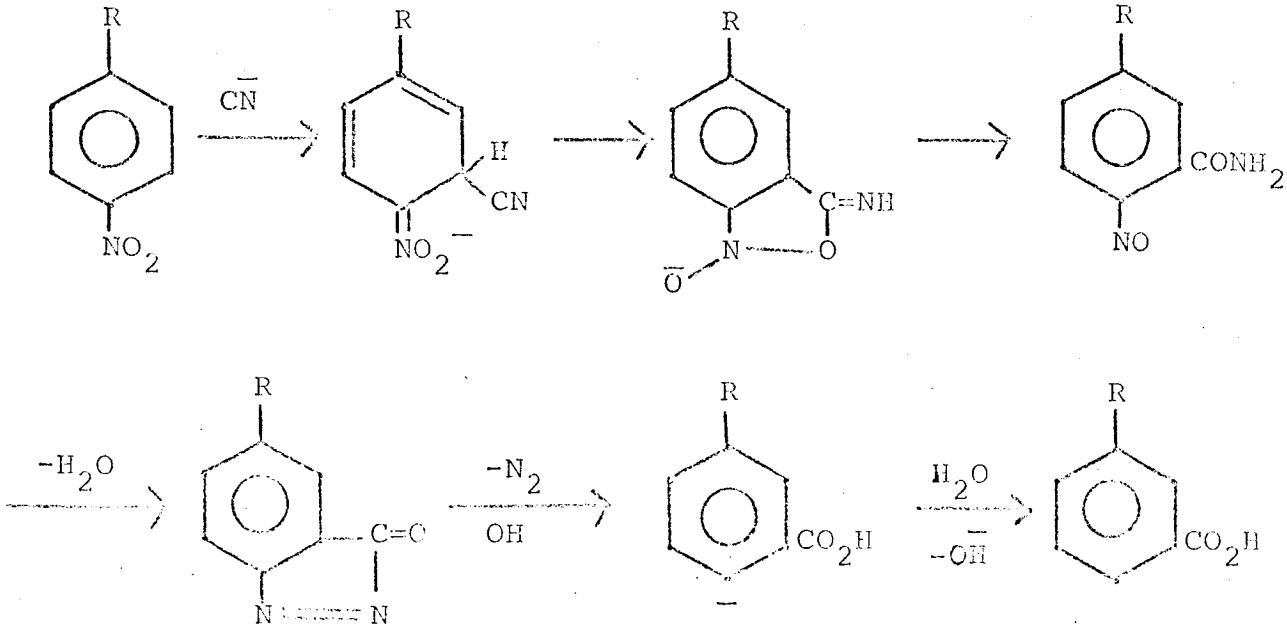
(107)

An intramolecular transfer of oxygen from the nitro group to nitrogen attached at the ortho-position is required in both the pyrolytic and the photolytic transformation of o-nitrophenyl azide into benzfuroxan (116) (equation 108), cf. B.16.



(108)

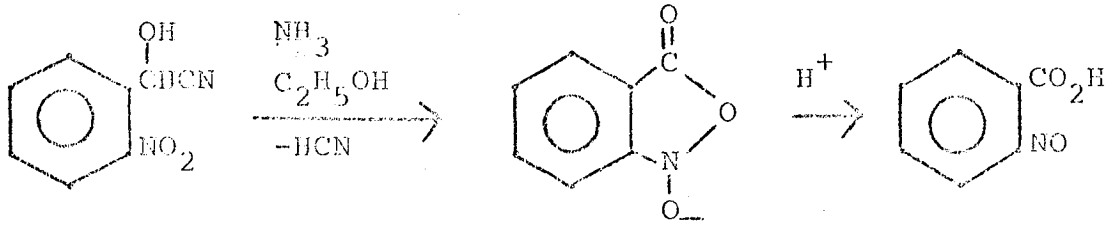
A derivative of o-nitrosobenzamide is a probable intermediate in the von Richter reaction whereby an aromatic nitro compound is transformed by aqueous alcohol containing an alkali cyanide into an aromatic acid in which the carboxyl group occupies a position ortho to the position from which the nitro group was ejected (183) (equation 109). o-Nitrosobenzamide,



(109)

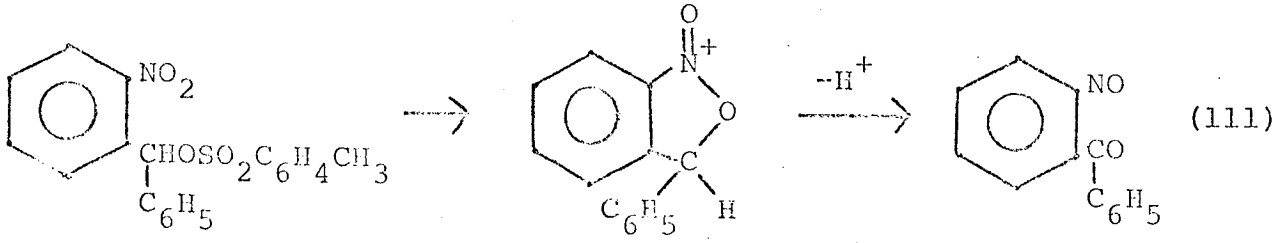
independently prepared, underwent the required reaction with both aqueous hydroxide and cyanide ions with the formation of benzoic acid (184).

An explanation for the transformation of o-mandelonitrile by treatment with ammonia into o-nitrosobenzoic acid, first reported in 1906 (185) and of o-nitrobenzaldehyde by treatment with potassium cyanide into the same product (186) may now be given an explanation similar to Rosenblum's mechanism for the von Richter reaction (equation 110). A similar reaction was



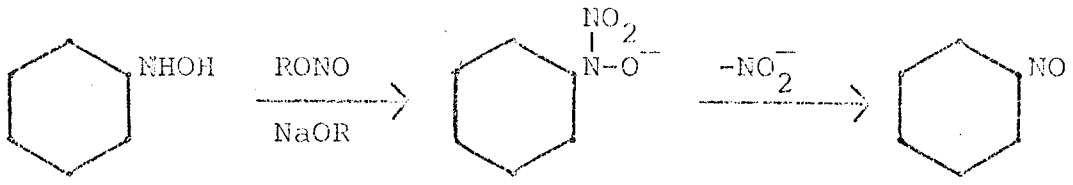
(110)

found in the formation of o-nitrosobenzophenone on treating 2-nitrobenzhydrol with p-toluenesulfonyl chloride in pyridine for which the following explanation was offered (187) (equation 111).

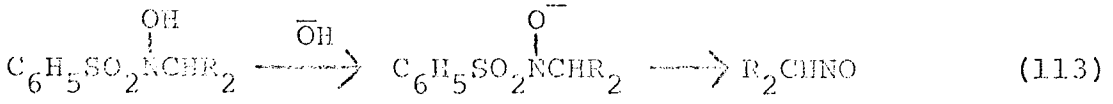


(111)

The step in which a nitroso group is generated in equations 93, 109, 110 and 111 and probably in equations 104, 106 and 107 requires opening of an isoxazoline ring, cf. B.24. When this derivative is also a cyclic hydroxamate anion (109 and 110) there is an analogy with the dissociation of linear hydroxamate anions (182) (equations 112, 113).



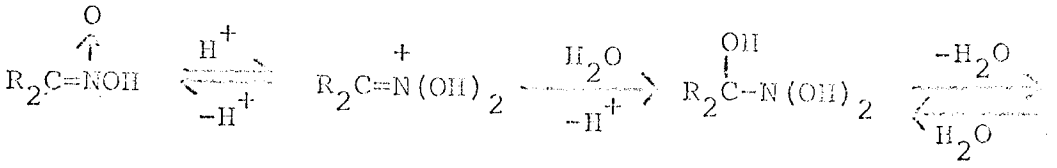
(112)

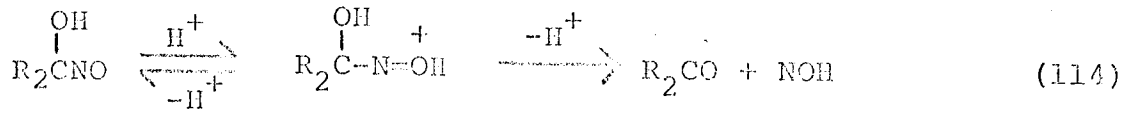


(113)

23. Nef reaction

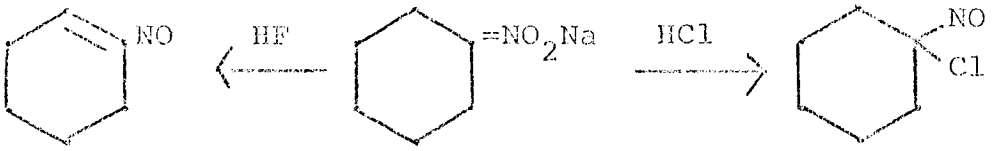
Hydrolysis of aci-nitroalkanes, the Nef reaction, is often utilized as a preparative method for carbonyl compounds. A persistent blue color in the reaction mixture during the time that aci-nitroalkane is being destroyed indicates the presence of a nitroso group. A reasonable mechanism for the Nef reaction in which α-hydroxy nitrosoalkanes are intermediates has been proposed (189, 190) (equation 114).



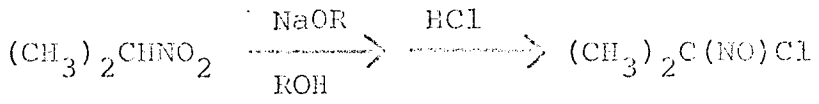


(114)

Isolation of an α-hydroxynitrosoalkane has apparently not been realized; however the reaction carried out in cold hydrochloric acid has led to the formation of α-chloronitrosoalkanes (191) (equations 115, 116).

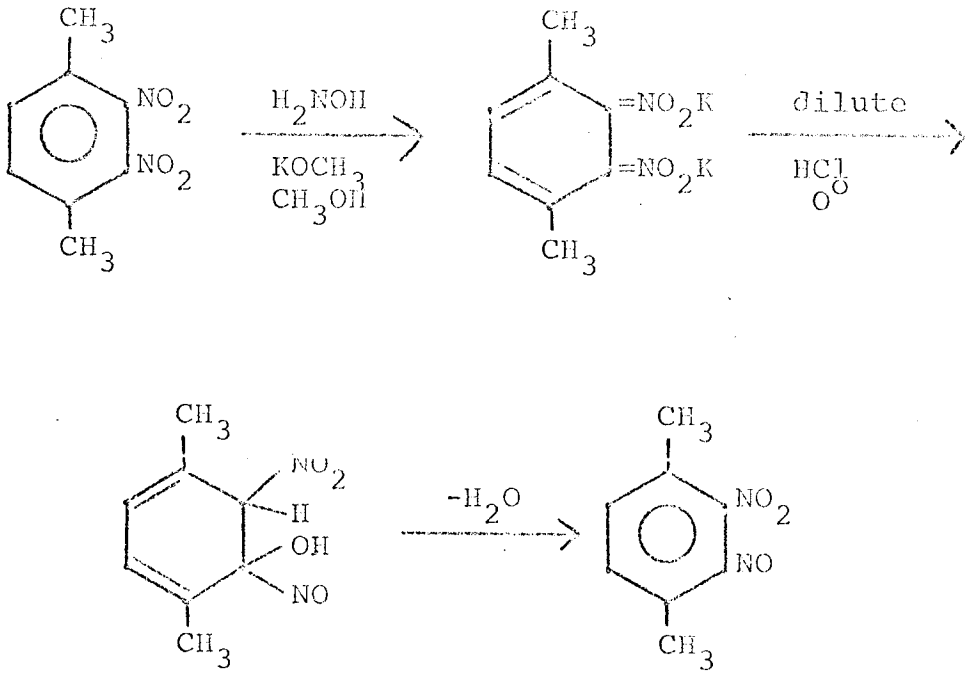


(115)



(116)

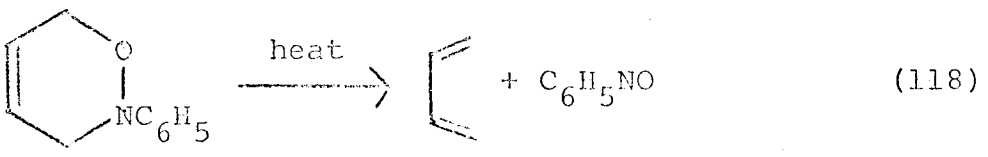
The second step in the formation of 2-nitroso-3-nitro-p-xylene from the corresponding dinitro compound by reduction followed by treatment with aqueous acid appears to follow the Nef reaction up to the stage of an alternative dehydration with aromatization (192) (equation 117).



(117)

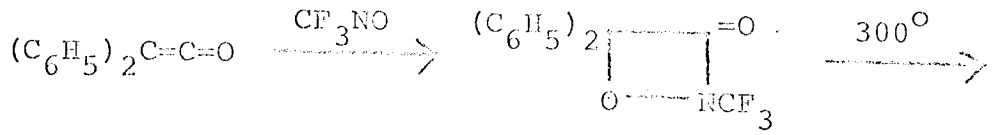
24. Pyrolysis of heterocycles

A few reports begin to indicate that saturated and certain partially saturated rings containing a ring oxygen adjacent to a ring nitrogen bearing an exocyclic substituent will undergo pyrolysis with the release of the corresponding nitroso compound. Both 3,6-dihydro- and tetrahydrooxazines will liberate nitroso compounds on heating (193) (equations 118, 119) and a similar reaction is known for a 4,4-diphenyloxazetidinone (194) (equation 120).



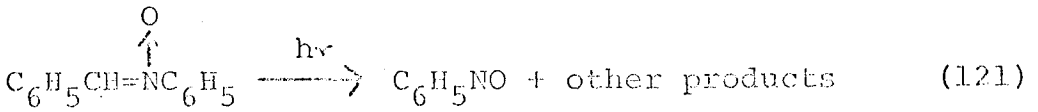
(118)

(119)

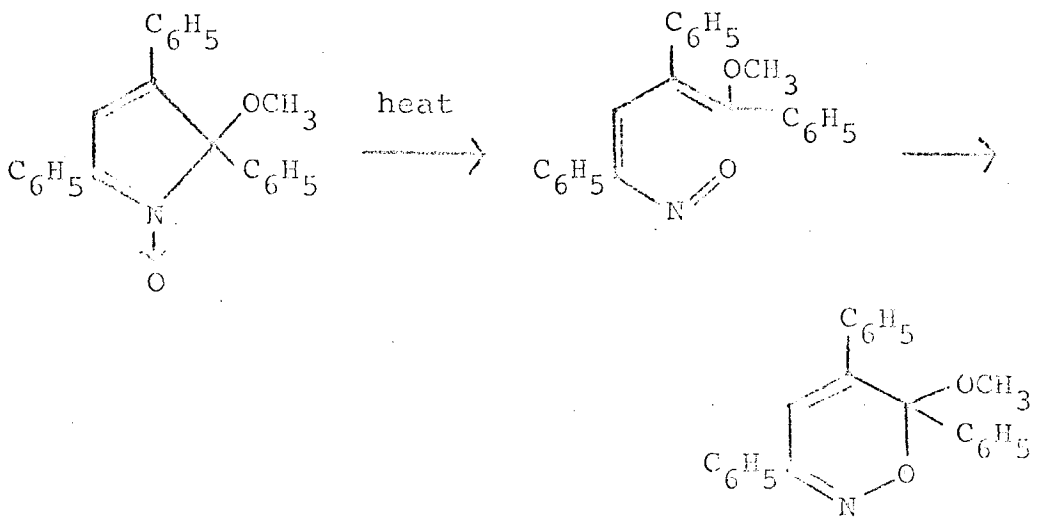


$$CF_3NCO + CF_3NO \qquad (120)$$

A prediction that certain five-membered heterocyclic N-oxides would undergo pyrolytic or photolytic ring-cleavage with the formation of a nitroso compound is based on the formation of nitrosobenzene from azoxybenzene by pyrolysis (195) and from N-phenylbenzalnitrone by photolysis (196) (equation 121) and the ring-opening of benzfuroxan, cf. B.16. An example may have been

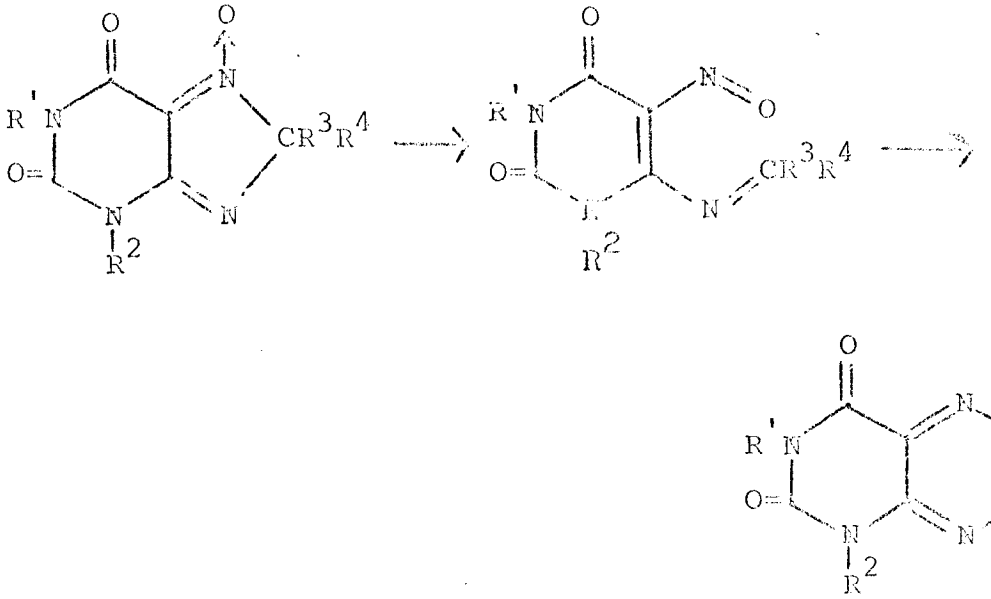


found in the pyrolytic transformation of 2,3,5- triphenyl-2-methoxypyrrole-N-oxide into the corresponding 1,2,6-oxazine (197). An attractive explanation based on the principles of valence isomerization requires ring-opening to a nitrosodiene followed by a new ring-closure (equation 122), cf. B.11.b. The facile



(122)

conversion of an imidazole-N-oxide into an oxadiazine (198) (equation 123) may also proceed by valence isomerization into a nitroso compound followed by a new ring-closure.



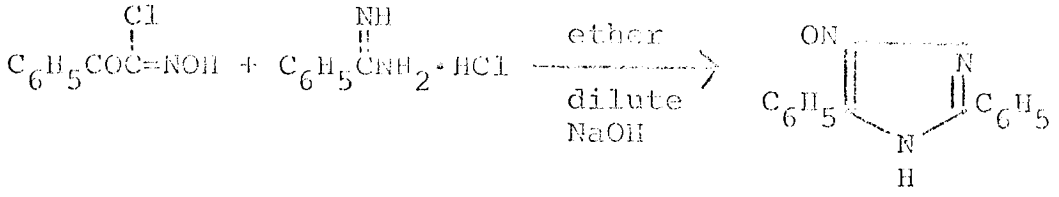
(123)

25. Electrolysis of oxime salts

A report that electrolysis of a 1:1 mixture of the oxime of mesoxalic ester and its sodium salt occurs with intermolecular coupling between the two α-carbon atoms and the formation of a 1,2-dinitroso derivative of an ethane (198) (equation 123) should be reinvestigated. In another report it is claimed that ketoximes undergo electrolytic oxidation in dilute sulfuric acid to give gem-nitronitroso compounds (199).

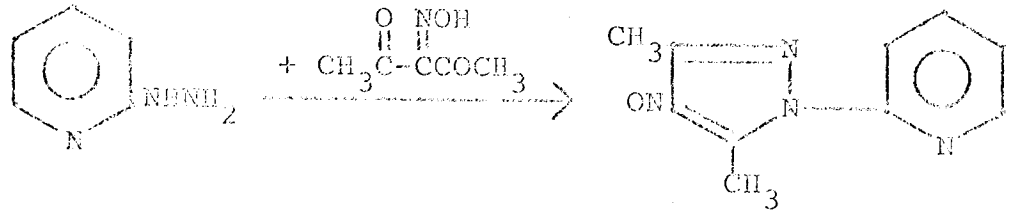
26. Condensation reactions

A variety of nitroso derivatives of heterocyclic aromatic compounds have been obtained by reactions in which the heterocyclic ring is produced by an intramolecular condensation. The following examples are illustrative (equations 124, 125, 126).



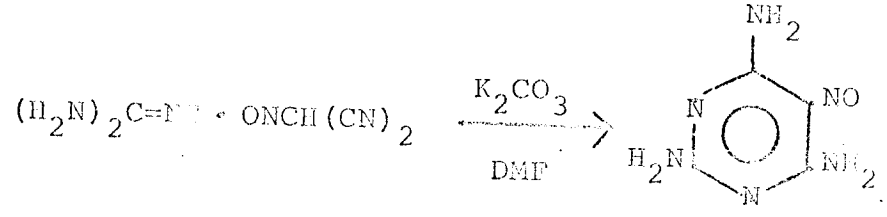
(124)

ref. 200



(125)

ref. 201



(126)

ref. 202

27. Nitroso compounds from diazo and diazonium compounds

Derivatives of diazoacetophenone in the presence of nitrosyl chloride release nitrogen and form geminal nitrosochloride adducts (203) (equation 127); however, it is not established that a carbene is an intermediate. Nitric oxide reacts with

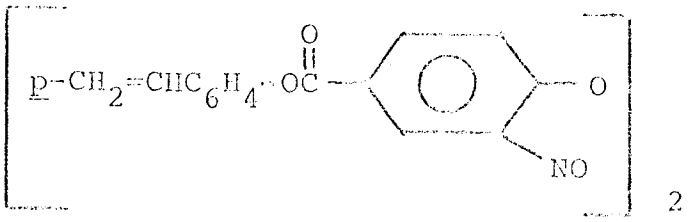
$$ArCOCHN_2 \xrightarrow{NOCl} ArCOCH(Cl)NO \longrightarrow ArCOC(Cl)=NOH \qquad (127)$$

diphenyldiazomethane to form a nitrimine (204) (equation 128) presumably by way of an iminoxy radical, $(C_6H_5)_2C=NO$, which has been detected (205). Nitrosobenzene has been prepared from the combination of phenyldiazonium chloride and an alkaline solution of potassium ferricyanide at 0° for 80 hours (206).

$$(C_6H_5)_2CN_2 \xrightarrow{NO} (C_6H_5)_2C=NNO_2 \qquad (128)$$

28. Natural occurrence

Aromatic nitroso compounds have been isolated as animal metabolic intermediates from corresponding aromatic primary amines and from corresponding aromatic nitro compounds (207, 208, 209). Bacterial degradation of p-nitrobenzoic acid to p-aminobenzoic acid apparently requires the intermediacy of p-nitrosobenzoic acid (210). The green pigment ferroverdin is obtained from a species of Streptomyces (211).



Ferroverdin

C. Structure and Reactions

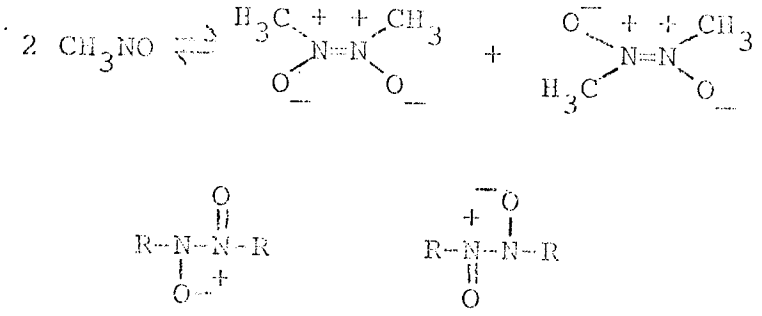
1. Dimerization

The diamagnetism for C-nitroso compounds was first demonstrated in a measurement of the magnetic susceptibility of nitrosobenzene and its p-dimethylamino derivative (212). Recently the first example of paramagnetic resonance absorption for a C-nitroso compound was reported for 1-acetoxy-2-methyl-2-nitrosopropane (colorless solid) in a 0.1M solution (blue) in toluene. The solution contained about six percent of a biradical presumably derived from a dimer. An e.s.r. signal was not obtained in similar investigations on p-nitrosotoluene, 2-chloro-2-nitrosopropane and 1-chloro-1-nitrosocyclohexane (213).

A tendency toward dimerization is a distinctive property of the nitroso group when attached to carbon. It is intimately associated with, and usually detected by, the disappearance of the blue or green color which originates from an $n \longrightarrow \pi^*$ transition with weak absorption in the 6300-8300 A^{O} range (ϵ=1 to 60) and is characteristic of the monomer. Many, but by no means all, examples are colorless or pale yellow dimers in the solid state,

becoming monomeric on melting, in the gas phase, or in solution. Two types of dimers are known; one is an N,N'-azodioxide, the other is an N,N-diperfluoroalkyl-O-nitrosohydroxylamine. There is no known example of a monomer which gives both dimers.

Nitrosomethane dimer has the structure of cis- and trans-N,N'-dioxoazomethane (214) (equation 129). Each configuration may be represented with additional resonance structures as shown.



(129)

When they will dimerize, nitroso derivatives of alkanes, alkenes, presumably alkynes, and aromatic compounds follow the pattern set by nitrosomethane and yield the expected dioxide of an azo compound. This dimer structure is well established by both chemical and physical evidence (215) but primarily by x-ray crystallography (216). Reduction of the dimer of α-nitroso-toluene to N,N'-dibenzylhydrazine by aluminum amalgam (217), its acid hydrolysis into benzhydrazide (218) and the formation of tetrahydropyridazines from nitroso dimers and dienes (c.13.)

clearly demonstrate the dimer N-N bond. In general, mixed dimers are unknown; however an incompletely characterized mixed dimer from a nitrosoheptane and 4-nitroso-1-octanol has been reported (219). There continues to be attempts to refine the description of the bonding and recently bond orders of 3/2 were considered for the dimer ONNO system (220).

A greater thermodynamic stability by about 25 kcal/mol for nitrosoparaffin dimers with respect to corresponding monomers is diminished and monomers are stabilized when electron-withdraving groups are attached at the α-position (221), e.g. the blue monomer, 2-bromo-2-nitrosopropane, gives no indication of dimerization (222).

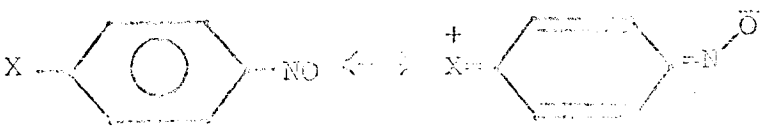
Monomers of nitrosoaromatic derivatives may be stabilized by resonance. Presumably this accounts for the dissociation of nitrosobenzene dimer in benzene occurring too rapidly to be measured (222). Conjugation between an electron releasing substituent in the para-position and the nitroso group further enhances the stability of the monomeric form of nitrosobenzene with respect to its dimer (223, 224). This effect is most pronounced in p-dimethylamino- and p-iodonitrosobenzene which are blue solid monomers (223) and in p-nitrosoanisole (225) and p-bromonitrosobenzene (223) which are blue solid monomers under some conditions.

Stabilization of the dimeric form relative to monomeric derivatives of nitrosobenzene is brought about by ortho-substitution and is most pronounced when both ortho- positions

are occupied by groups larger than hydrogen. A spectrophotometric study of the monomer-dimer equilibrium in benzene for a series of derivatives of 2,6-dichloronitrosobenzene demonstrated that an electron releasing substituent at the 4-position favors dissociation to the monomer. That dimer dissociation is electron-demanding was indicated by a ρ value of -1.5, obtained in the usual Hammett ρ-σ treatment. A change in σ_p^O gave a measure of the "resonance effect" of the 4-substituents ($CO_2C_2H_5$, H, CH_3, Cl, Br and OCH_3) which was found to be identical with the isoelectronic derivatives of benzaldehyde as determined from the reversible formation of derivatives of benzaldehyde cyanohydrin (224).

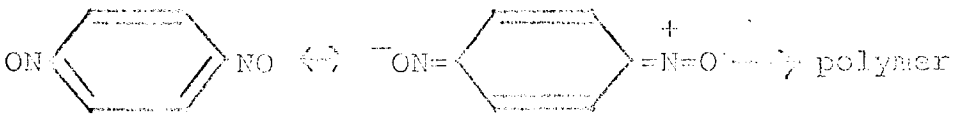
A postulated dimerization by an ionic reaction (223) (equation 130) is in agreement with the resonance structures (equation 131) in which the nitroso group is electron withdrawing. The ortho- effect may be attributed to steric inhibition of resonance in the monomer (226) or to a stabilization of the dimer through steric inhibition of resonance resulting in a stronger N-N bond (more nearly a double bond) (215, 227). In contrast with

$$R\text{-}\ddot{N}\text{=}\ddot{O} + R\text{-}\overset{+}{\ddot{N}}\text{-}\overset{-}{\ddot{O}}: \longrightarrow (RNO)_2 \qquad (130)$$



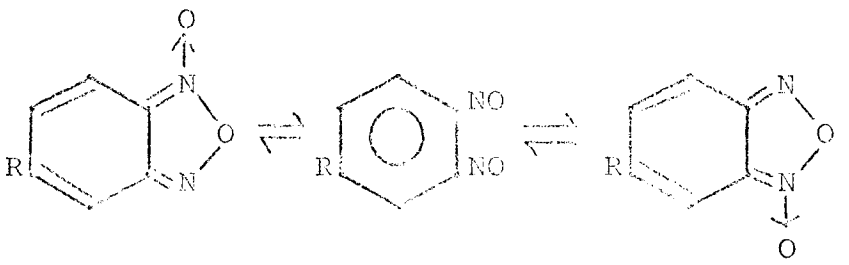
(131)

p-nitronitrosobenzene which is a pale yellow solid dimer, p-dinitrosobenzene when freshly sublimed is a green solid monomer. It rapidly changes to a pale yellow polymer (228) (equation 132).



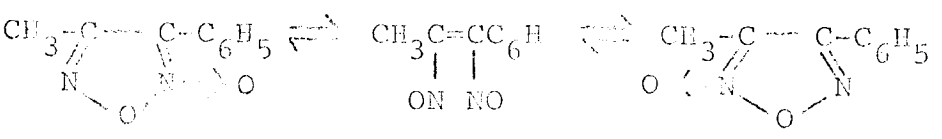
(132)

Dimerization may be eliminated if intramolecular interaction between the nitroso group and an o-substituent in an aromatic compound may occur. o-Dinitrosobenzene has been a postulated intermediate (229) in the equilibration of unsymmetrically substituted benzfuroxans (230) (equation 133). A dimer of o-dinitrosobenzene is unknown. In a very similar equilibrium,



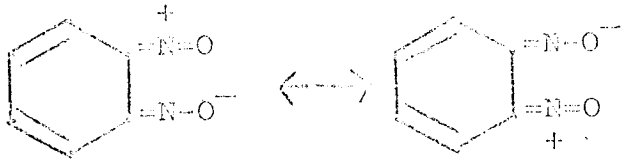
(133)

dinitrosoolefins are assumed intermediates in the pyrolytic isomerization of unsymmetrically substituted monocyclic furoxans (230) (equation 134). In each example (equations 133, 134) the



(134)

intermediate may exist as zwitterionic resonance structures (equations 135, 136).



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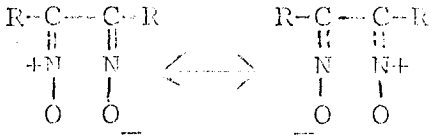
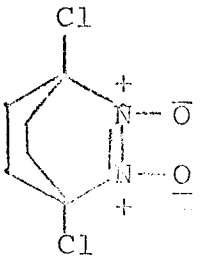


(136)

In general dimers of nitrosoalkanes are more stable in the trans- configuration (214). Certain cyclic azo-N,N'-dioxides are allowed only in the cis- configuration, e.g., the azodioxides (3, 4, 5) from ring-closure of 1,4-dichloro-1,4-dinitrosocyclohexane (116), 2,2'-dinitrosobiphenyl (116) and 4-methylcinnoline-1,2-dioxide (231). Dissociation of the "internal nitroso dimers" which are also cinnoline dioxides has not been demonstrated, in contrast with the ring-opening of furoxans, vide supra.



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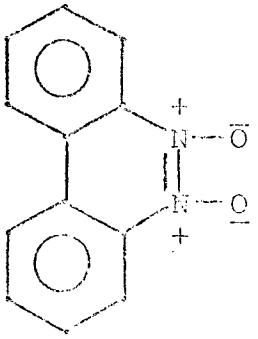

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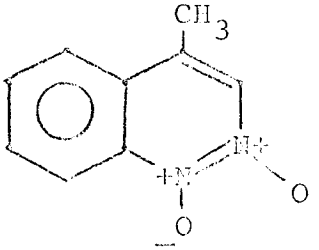


5

Nitrosobenzene dimer exists in the cis-configuration but its p-bromo derivative is a trans-dimer. Apparently an example of a dimer of a nitrosoaromatic compound in both cis- and trans-configurations has not been reported (231). Conversion of a trans-nitrosoalkane dimer to the cis-isomer may be brought about by ultraviolet irradiation; the reverse process occurs readily in nonpolar solvents without irradiation (214). Similarities in solvent effects for both the conversion of cis- to trans- dimers and the dissociation of dimers suggests the intermediacy of the corresponding monomers in dimer isomerization.

The other known mode of dimerization is a photochemical reversible reaction and may be illustrated with trifluoronitrosomethane (232) (equation 137). There is no tendency for dimerization to occur in the dark, even after several years, but on exposure to light (particularly ultraviolet light) the blue gas changes almost quantitatively into a brown-red gas shown to be the dimer. The reaction apparently proceeds with the formation

$$2\ CF_3NO \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (CF_3)_2NONO \qquad (137)$$

of the radicals, trifluoromethyl and nitric oxide which then add to unchanged monomer, cf.C.8. A dimer of β-chlorotetrafluoronitrosoethane has been obtained from the combination of

nitric oxide and the stable di-β-chlorotetrafluoroethyl nitric oxide (233) (equation 138).

$$(ClCF_2CF_2)_2NONO \rightleftharpoons (ClCF_2CF_2)_2NO + NO \qquad (138)$$

2. Isomerization to oximes

The nitrosation of aliphatic carbon atoms is an important preparative method for oximes (isonitroso compounds in the older literature) in which the intermediate nitroso derivative may or may not be isolated. Isomerization to the oxime, in the gas phase, with melting or in a solution, may occur more rapidly than dimerization, and is catalyzed by polar solvents, strong acids and bases and nitric oxide (231). It is apparently irreversible (equation 139). When the nitrosating agent is nitrous fumes (N_2O_3) and the reaction is carried out in ether, the intermediate

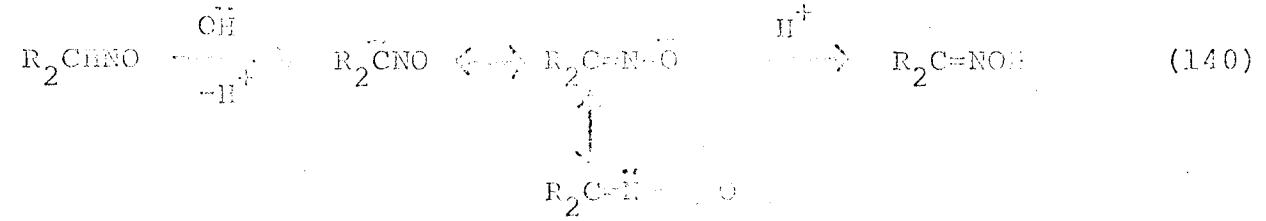
$$R_2CHNO \longrightarrow R_2C{=}NOH \qquad (139)$$

nitroso compound may be isolated (234). The first-order vapor phase isomerization of nitrosomethane, complicated by a contribution from a surface reaction, apparently proceeds by an intramolecular hydrogen transfer in agreement with a high negative entropy of activation (235).

As the molecular weight increases, the rate of isomerization may decrease as is seen in the increasing resistance toward

isomerization for RNO in the series R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$ (236). A particular interest may be found in α-nitrosotoluene which partially isomerizes into benzaldoxime on formation by the oxidation of benzylhydroxylamine with dichromate but is predominantly transformed into an extraordinarily stable nitroso dimer (218). When treated with hydrogen chloride in chloroform it is converted to a mixture of benzhydrazide and its benzylidene derivative, both of which have retained linked nitrogen atoms (218). Based on this information, it would appear probable that the conversion of certain nitrosoalkane dimers into corresponding oximes requires the intermediacy of the monomer, in agreement with the rearrangement of secondary nitroso dimers in the presence of hydrogen chloride which is dependent only on dimer concentration suggesting that the rate-determining step is likely to be dissociation to monomer (237).

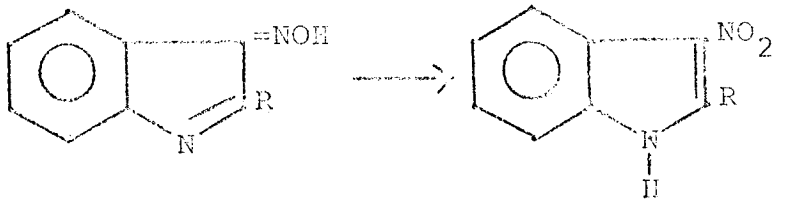
It may be assumed that the base catalyzed isomerization of a nitroso monomer to the corresponding oxime proceeds by the initial abstraction of a proton from the α-carbon atom. It would then appear that the resulting carbanion exists in resonance with an oximino anion (equation 140); however, available chemical evidence indicates that this anion reacts with cations only at



(140)

oxygen and/or nitrogen. An analagous resonance structure for the iminoxy radical (B.15.) in which the unpaired spin density resides on oxygen and nitrogen and not on carbon has been described. This problem of electron density distribution may be extended to the interesting nitrosolate anions, $R-\underset{\underset{NO}{|}}{C}=NO^-$.

Available information does not answer either the questions on the equivalence of the nitrogen atoms and of the oxygen atoms or the question of alkylation at carbon. Apparently gem-dinitroso compounds of the type $R_2C(NO)_2$ where $R \neq H$ are not known. A striking example of oxime stability with respect to its nitroso isomer is found in an indolonoxime. Its reactions, e.g., permanganate oxidation to the corresponding 3-nitroindole, do not require the intermediacy of a nitroso isomer (equation 141). Indeed 3-nitrosoindoles are unknown except in certain examples where the ring nitrogen carries a substituent. β-Nitrosopyrroles give a fleeting green color on liberation from their salts but rapidly change to yellow, presumably indicative of the isomeric oximinopyrrolenine structure (238) (equation 142).



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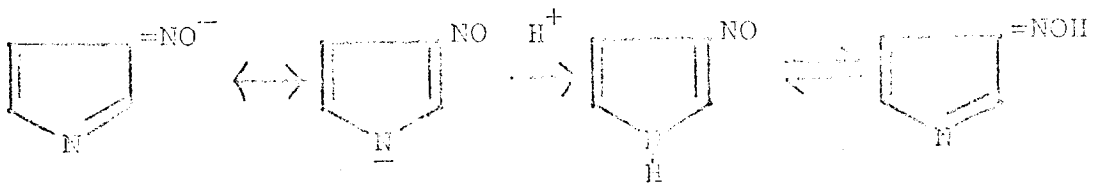
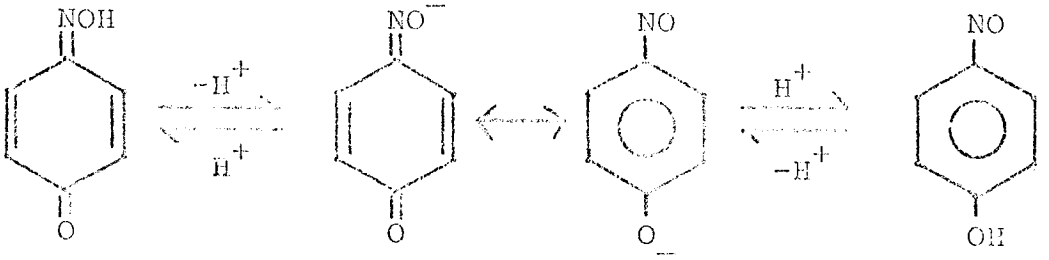


(142)

An equilibrium between o- and p-nitrosophenol with the respective quinone monoxime is well established. In solutions, p-nitrosophenol (about 15%) and p-benzoquinone monoxime (about 85%) are detected by analysis of spectroscopic data (239) (equation 143). The isomers are isolated in two crystalline forms, one is pale green, the other is colorless. Alkaline solutions give a reddish-green color. A similar bright red anion was obtained from the oxime of phthalic anhydride (240) (equation 144).



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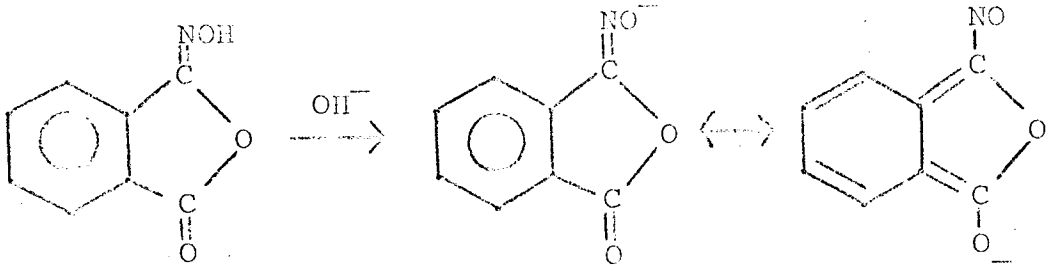
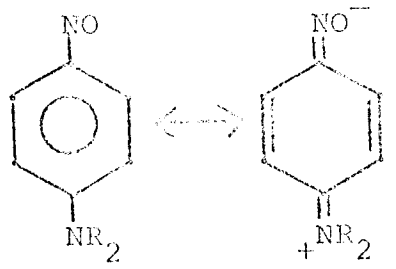


(144)

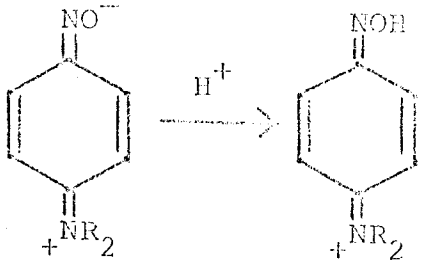
3. Nitrosoaromatic amine zwitterions

A contribution from a resonance zwitterionic structure assigned to primary, secondary and tertiary p-aminonitrosobenzene derivatives (equation 145) is reminiscent of a similar expression for p-dinitrobenzene, cf.C.1. It readily provides a basis for

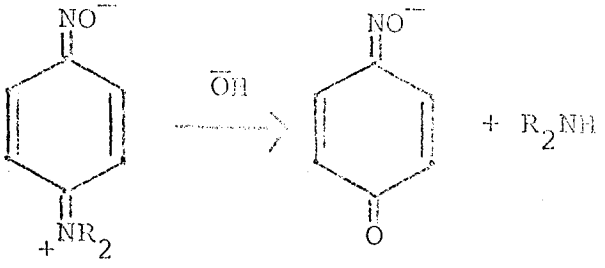


(145)

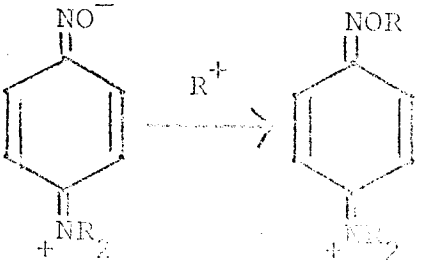
explaining reactions with acids and bases and alkylations (equations 146, 147, 148) and accounts for the high dipole moment of p-nitrosodimethylaniline (218, p. 220).



(146)

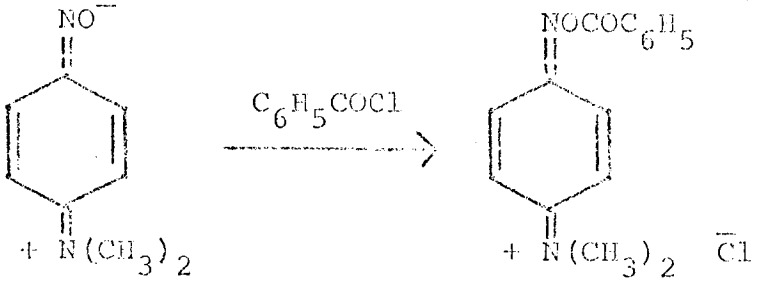


(147)



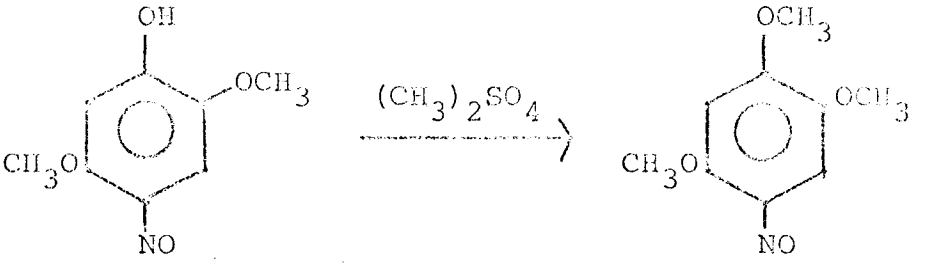
(148)

Alkylation (equation 148) occurs at oxygen rather than at amine nitrogen (see equation 145) as is seen from the product which on hydrolysis gives a dialkyl, rather than a trialkyl, amine (241). It has been reported that acylation also occurs at oxygen (242) (equation 149). In contrast nitrosophenols may alkylate at the



(149)

phenolic oxygen as is seen in the formation of 2,4,5-trimethoxynitrosobenzene from 2,5-dimethoxy-4-hydroxynitrosobenzene and dimethyl sulfate (243) (equation 150).



(150)

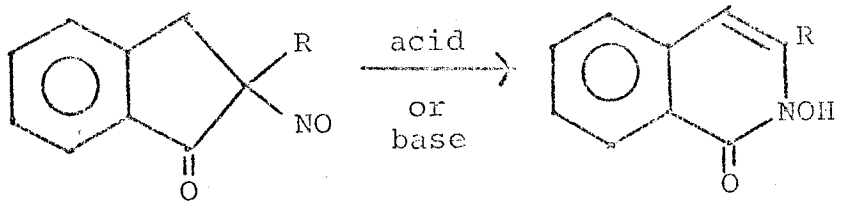
4. Activation of other substituents

A substituent other than hydrogen may be labile at the α-position. In mild acid treatment, 2-acetyl-2-nitrosopropane loses the acetyl group (244) (equation 151). A similar reaction in base has been reported for the benzoyl analog (245) (equation 152).

$$(CH_3)_2C(NO)COCH_3 \xrightarrow[H_2O]{H^+} (CH_3)_2C{=}NOH + CH_3CO_2H \qquad (151)$$

$$C_6H_5COC(CH_3)_2 \xrightarrow[CH_3OH]{^-OCH_3} C_6H_5CO_2CH_3 + (CH_3)_2C{=}NOH \qquad (152)$$
(NO)

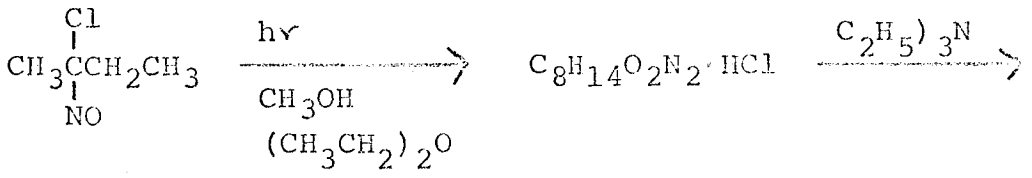
The ring-expansion of 2-alkyl-2-nitroso-1-indanones to isocarbostyril derivatives may follow a related path (245) (equation 153).

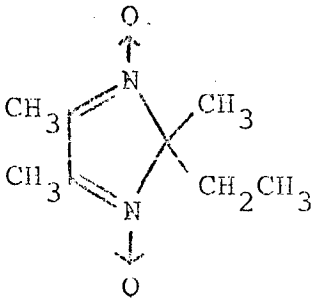


An incompletely understood acid hydrolysis converts 2-chloro-2-nitrosobutane into a mixture of the oxime of butanone-2 and the monoxime of butanedione-2,3 (246) (equation 154). It has been

$$CH_3\overset{\overset{Cl}{|}}{\underset{\underset{NO}{|}}{C}}CH_2CH_3 \xrightarrow[H_2O]{\text{acid}} CH_3\overset{\overset{NOH}{\|}}{C}CH_2CH_3 + CH_3\overset{\overset{NOH}{\|}}{C}OCCH_3 \qquad (154)$$

suggested that these two oximes are first formed in the photolytic transformation of the geminal nitrosochloride into an imidazole-di-N-oxide (246) (equation 155).

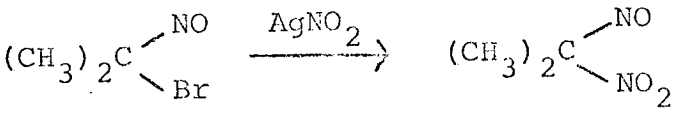




(155)

Aliphatic carboxylic acids in oleum are nitrosated at the α-position and decarboxylated on treatment with nitrosyl sulfuric acid, cf.B.10. When α-hydrogen is present decarboxylation from an oxime would account for the product, an aldoxime (247); but in the nitrosative decarboxylation of an aromatic acid decarboxylation from a tertiary nitroso compound is proposed, cf.B.10.

There is at least one example of α-halogen displacement (248) (equation 156). The electron-withdrawing power of the nitroso

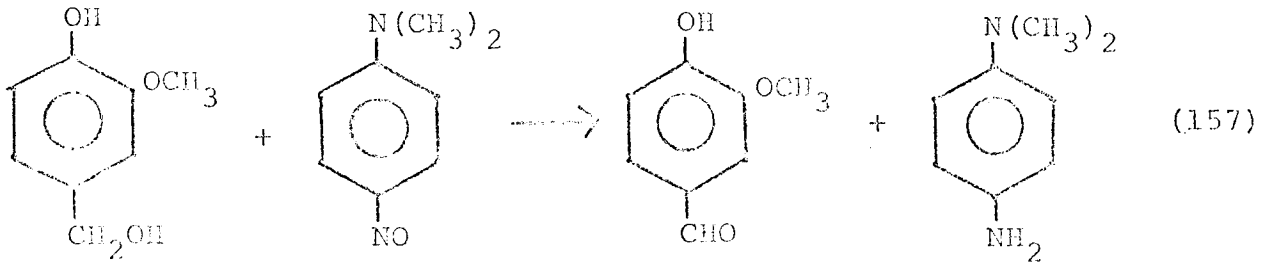


(156)

group has been demonstrated with p-bromonitrosobenzene which reacts more rapidly with silver nitrate solution than p-bromonitrobenzene does (249).

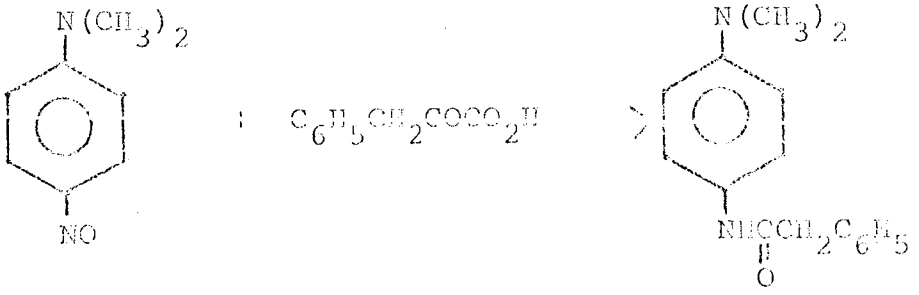
5. Reduction

Over platinum (250), nickel (251), palladium (252) and other catalysts, aliphatic and aromatic nitroso compounds are generally reduced to primary amines. A reported incomplete reduction with the formation of cyclohexylhydroxylamine from nitrosocyclohexane dimer over a catalyst is exceptional (253). Metal and acid combinations and certain lower valent metal salts also give reduction to the corresponding amine. Common examples include tin in hydrochloric acid or stannous chloride (254, 255) or zinc dust in acid (256). Concentrated hydrochloric acid both reduces and halogenates nitrosobenzene to form chloroazoxybenzene, trichloroaniline, chlorophenylhydroxylamine and other products (257). Sodium bisulfite reduced p-nitrosotoluene to p-toluidine and also sulfonated the ring (258). Hydroiodic acid transformed p-nitrosodimethylaniline into p-aminomethylaniline by simultaneous reduction and demethylation (259). Oxidation of vanillyl alcohol to vanillin may be brought about with p-nitrosodimethylaniline (260) (equation 157). Phenylpyruvic



(157)

acid (261) and N-benzyl-1,4-dihydronicotinamide (262) also reduce p-nitrosodimethylaniline to a primary amine (equation 158) but pyruvic acid reduces the nitroso compound to the corresponding azoxy derivative (261).

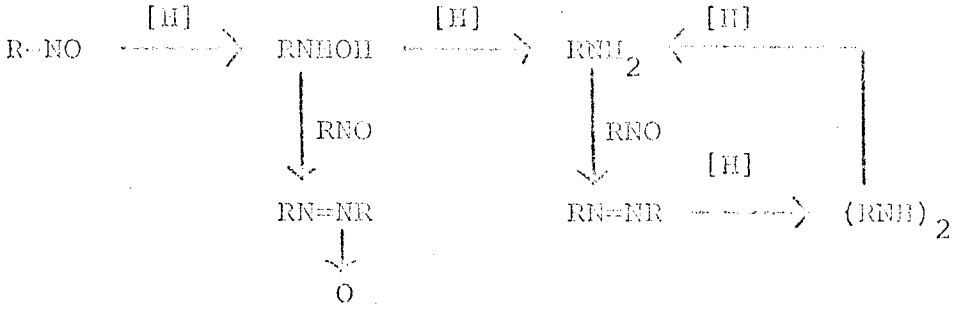


(158)

With varying degrees of control over product formation aromatic nitroso compounds are reduced to mixtures of amines, azo, azoxy and hydrazocompounds by alcoholic alkali or alkoxide (263), formaldehyde (264), hydrazine (265), formamide (266), hydrogen sulfide (267), trivalent molybdenum (268), zinc diethyl (269), arsenites (270), sodium borohydride (271), phenyl mercaptan (272), lithium aluminum hydride (273) and other reagents. A deficient amount of lithium aluminum hydride transforms nitrosobenzene into diphenylnitric oxide, detected and identified by its e.s.r. spectrum (273). The photoreduction of nitrosobenzene in methanol, ethanol or benzene gives primarily azoxybenzene but also its p-nitro-, o-hydroxy and p-hydroxy derivatives, diphenylamine and nitrodiphenylamines (274, 275). Each of these latter

two methods of reducing nitrosobenzene require cleavage and reformation of a C-N bond. An enzymatic reduction of p-nitrosobenzoic acid to p-aminobenzoic acid has been observed (276).

A summary of the reduction paths is helpful (277) (equation 159). With each example isomerization of the nitrosoalkane to an oxime may be more rapid than reduction and, if so, will alter the course of the reduction (equation 160).



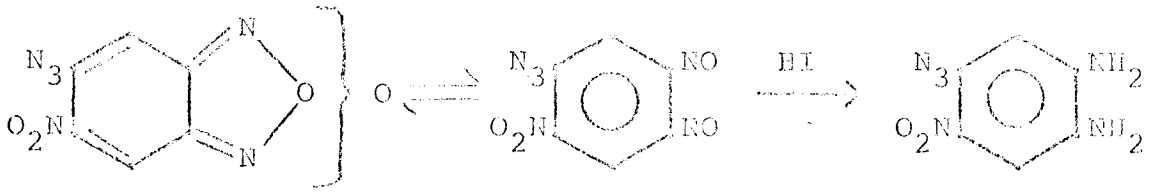
(159)

$$R_2CHNO \longrightarrow R_2C{=}NOH \xrightarrow{[H]} R_2CHNHOH \xrightarrow{[H]} R_2CHNH_2 \qquad (160)$$

Reductive allylation transforms nitrosobenzene into N,N-dipropylaniline in a reaction with propionaldehyde and hydrogen over nickel (278). Ketones require more drastic treatment.

Hydroxylamine reduces both o-dinitrosobenzene (benzfuroxan) and its para- isomer to the corresponding dioximes (116, 279). The sensitivity of nitroso groups toward reduction is revealed in the transformation of 1,2-dinitroso 4-azido-5-nitrobenzene by hydrogen iodide into 1,2-diamino-4-azido-5-nitrobenzene

(280) (equation 161). Copper in the presence of an acid reduces o dinitrosobenzene, cf.C.15., to o-nitroaniline and [illegible]



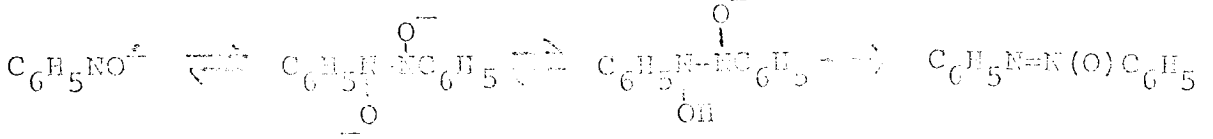
(161)

2 structures

o-benzoquinone dioxime into the same product (281). A similar over-all reduction of the sodium salt of the bisulfite adduct of 1,2-dinitrosonaphthalene-6-sulfonic acid in dilute sodium carbonate solution to a disodium salt of 1-amino-2-nitronaphthalene-4,6-disulfonic acid has been observed (282).

Aromatic thiolate anions and the t-butoxide anion transform nitrosobenzene into its radical anion as determined by e.s.r. measurements (283) (equation 162) and is the first step in the reduction of nitrosobenzene to azoxybenzene (284) (equation 163).

$$C_6H_5NO \xrightarrow{B^-} C_6H_5NO^{\cdot-} \qquad (162)$$



(163)

Aromatic nitroso compounds react with sodium in ether to produce $[ArNO]^{\cdot-}Na^+$, $[ArNO]_2^{=}2Na^+$ and $ArN(ONa)_2$ (285) and similar results have been obtained with lower valent aluminum and unipositive magnesium (286).

The radical anion of nitrosobenzene is also formed in the first polarographic reduction step conducted in 0.2N sodium nitrate in dimethylformamide. When oxygen is present nitrobenzene is formed whereas in the absence of oxygen, azoxybenzene is the final product (287). The reversible reduction of nitrosobenzene to phenylhydroxylamine is a two-electron process (288, 289) in which the redox potential varies with pH. The variation of the half-peak potential (vs. S.C.E.) over a pH range from 1.6 to 12.5 at 25° is given by $E_{1/2}=0.33 - 0.060$ pH (290).

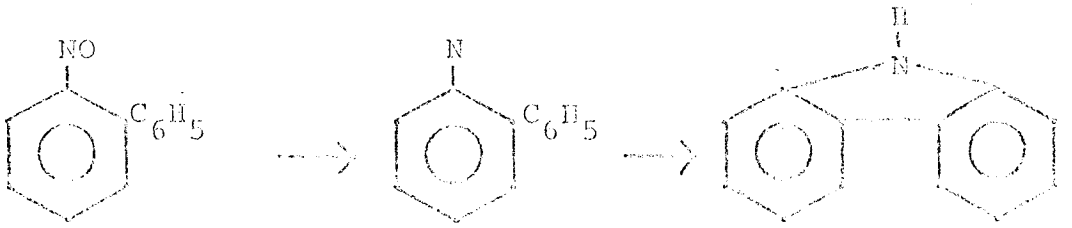
6. Deoxygenation

Deoxygenation of a nitroso compound may provide a nitrene intermediate. An explanation for the formation of azoxybenzene on treating nitrosobenzene with triphenylphosphine requires deoxygenation to phenyl nitrene and subsequent combination with nitrosobenzene (291) (equation 164). In other examples the nitrene may prefer an intramolecular reaction. Cyclization of o-biphenyl

$$C_6H_5NO + (C_6H_5)_3P \longrightarrow C_6H_5N + (C_6H_5)_3PO$$

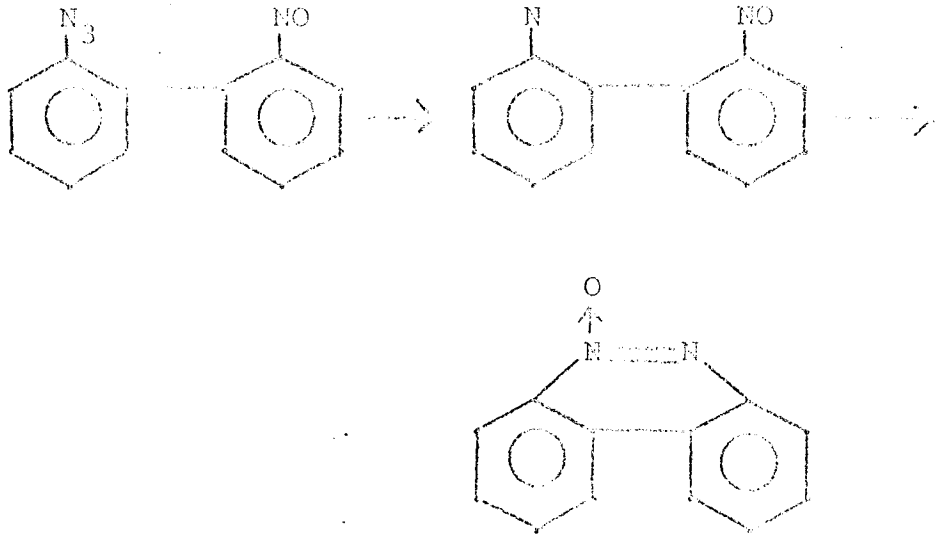
$$C_6H_5N + C_6H_5NO \longrightarrow C_6H_5N(O)NC_6H_5 \qquad (164)$$

nitrene, an assumed intermediate, accounts for the formation of carbazole in a reaction between o-nitrosobiphenyl and triphenylphosphine (282) (equation 165). The intermediacy of a nitrene



(165)

has been assumed in both the photolytic and the pyrolytic conversion of o-nitroso-o'-azido-biphenyl into benzocinnoline-N-oxide (293) (equation 166).



(166)

An isonitrile may deoxygenate a nitroso compound and apparently can combine with an intermediate nitrene with the formation of a

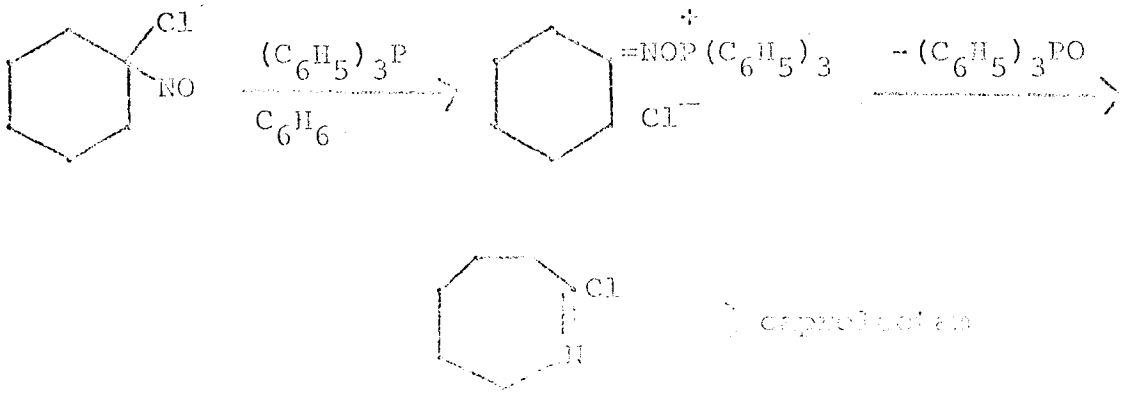
carbodiimide. N-Trifluoromethyl-N'-methylcarbodiimide is obtained from trifluoronitrosomethane and methyl isonitrile (294) (equation 167). The earlier work of Passerini (295) in

$$CF_3NO \xrightarrow[-CH_3NCO]{CH_3NC} CF_3N \xrightarrow{CH_3NC} CF_3N{=}C{=}NCH_3 \qquad (167)$$

which N,N'-diphenylurea was obtained from nitrosobenzene and phenyl isonitrile is easily accounted for by a similar reaction leading to the formation of diphenylcarbodiimide followed by hydration (equation 168).

$$C_6H_5NO \xrightarrow{C_6H_5NC} C_6H_5N{=}C{=}NC_6H_5 \xrightarrow{H_2O} C_6H_5NHCONHC_6H_5 \qquad (168)$$

Deoxygenation and ring-enlargement occur when gem-chloronitrosocyclohexane is treated with triphenylphosphine in benzene. An explanation which has been offered may not require the intermediacy of a nitrene (296) (equation 169).



(169)

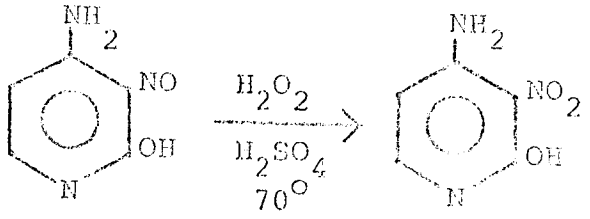
7. Oxidation

Nitric acid (297), hydrogen peroxide (298), permanganate (299) chromic oxide (300), persulfuric acid (300), ammonium persulfate (301), hypochlorite (300), peroxyacetic acid (302), peroxytrifluoroacetic (303), ozone (304) and other reagents oxidize nitroso compounds to nitro compounds. The reaction, generally limited to tertiary aliphatic and aromatic nitroso derivatives, often leads to several products. In strong nitric acid, nitrosobenzene is transformed into nitrobenzene, p-dinitrosobenzene, p-nitrophenol, 2,4-dinitro-phenol, picric acid and oxalic acid (305).

With first-order dependence on each reactant, nitrosobenzenes are oxidized by peroxyacetic acid in aqueous ethanol to corresponding nitrobenzenes (302). The reaction is accelerated by electron-releasing p-substituents and by changing the solvent from ethanol to water, and it is decelerated by electron-withdrawing p-substituents. Apparently a greater acidity in the peroxy acid enhances the reaction; peroxychloroacetic and Caro's acid each oxidize nitroso benzene more rapidly than does peroxyacetic acid. A mechanism consistent with these facts calls for a reaction initiated by a nucleophilic attack of the nitroso nitrogen on the outer oxygen of the peroxyacid with a transition state composed of the peroxyacid, the nitroso compound and a solvent molecule.

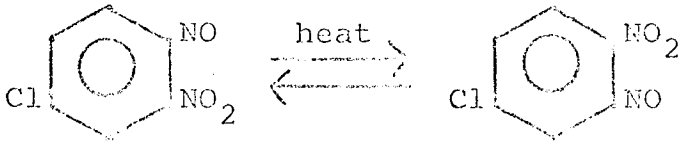
This mechanism is also supported by the direction and magnitude of the substituent effect (ρ -1.58), the activation parameters for nitrosobenzene (E_a 16.1 kcal mole^{-1}, $\Delta S^{\ddagger}$ -22 cal mole^{-1} deg^{-1}), and the absence of acid catalysis.

The resistance of m-trifluoromethylnitrosobenzene toward oxidation by permanganate, dichromate or hydrogen peroxide in acetic acid (306) is not typical and gives a striking contrast with the facile oxidation of the nitroso group in 2-hydroxy-3-nitroso-4-aminopyridine by hydrogen peroxide in sulfuric acid (307) (equation 170).

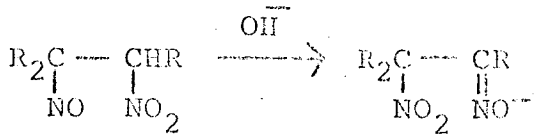


(170)

An intramolecular transfer of oxygen between nitroso and nitro groups ortho to each other in aromatic compounds or on adjacent parafinic carbon atoms is thermally produced in one instance and base-catalyzed in the other (equations 171, 172). The intermediacy of a furoxan oxide and a dihydro furoxan oxide respectively may be required (308, 309).



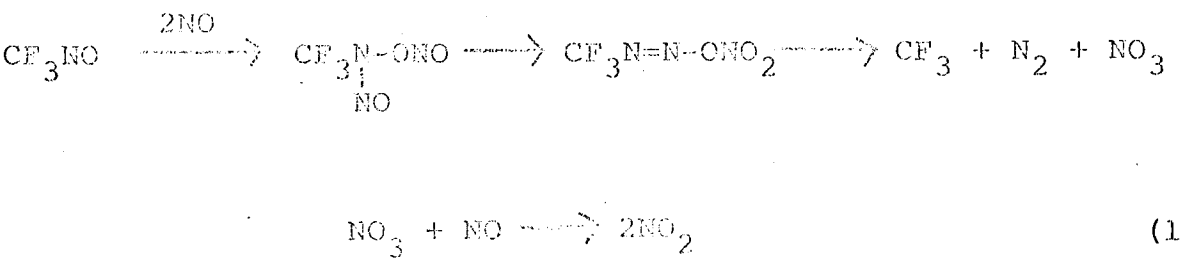
(171)



(172)

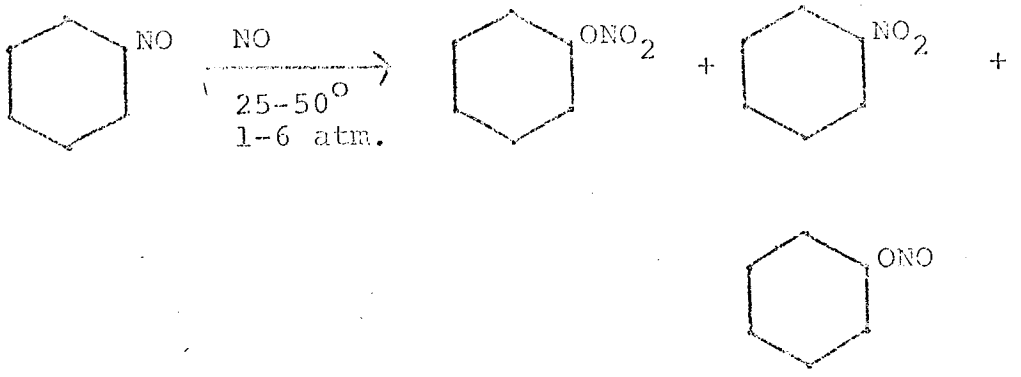
8. Free radicals

Free radicals tend to attack the nitroso group in pairs in a reaction leading to the formation of an O,N-disubstituted hydroxylamine. The adduct from trifluoronitrosomethane and two molecules of nitric oxide has been isolated (310); however, the reaction usually proceeds at higher temperatures with rearrangement to a diazonium nitrate and subsequent decomposition (311) (equation 173). Certain aliphatic nitroso compounds combine



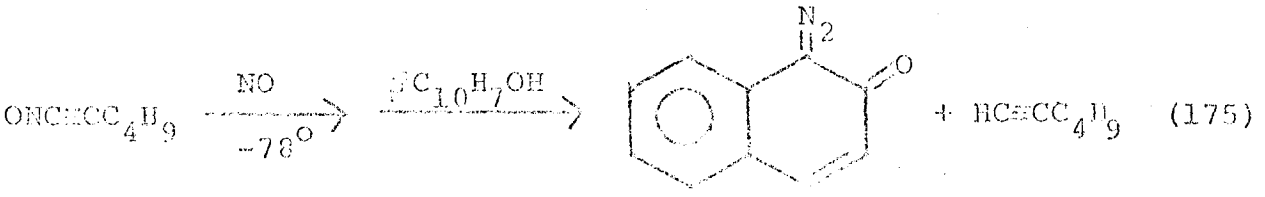
(173)

with nitric oxide to form corresponding nitro compounds and nitrate esters along with trace amounts of nitrite esters (312) (equation 174). Presumably, a dinitrosohydroxylamine and a diazonitrate are intermediates.



(174)

β-Naphthol is transformed into a diazooxide on addition to the reaction mixture in which 1-nitrosohexyne-1 is treated with nitric oxide in methylene chloride at low temperature (313) (equation 175). On similar treatment, dimethylaniline is transformed into its p-nitro and p-diazonium salt derivatives.



(175)

Many, but not all, radicals readily react with the nitroso group. Nitrosobenzene has an exceptionally high "methyl affinity" (ca 10^5) (314) but has less tendency to react with triphenylmethyl (315). It has been reported that nitrosobenzene reacts with triphenylmethyl in benzene to produce triphenylcarbinol and p,p'-ditriphenylmethylazoxybenzene (316). The formation of trimethylhydroxylamine from nitrosomethane and methyl radicals at room temperature has been demonstrated (317). In contrast,

apparently neither an O,N-dinitrosohydroxylamine nor a triperfluoroalkylhydroxylamine has been detected during the dimerization of a perfluoronitrosoalkane which presumably proceeds with the initial formation of a nitric oxide and a perfluoroalkyl with subsequent addition of each to an unchanged perfluoronitrosoalkane, cf.C.1. A radical mechanism was proposed to explain the formation of N-trifluoromethyl-N'-fluorodiimide oxide from either the photochemical or the thermal reaction of trifluoronitrosomethane and tetrafluorohydrazine (318) (equation 176).

$$RNO \xrightarrow{\cdot NF_2} R\overset{\overset{O^-}{|}}{\underset{+}{N}}\!-\!NF_2 \longrightarrow R\overset{\overset{O^-}{|}}{\underset{+}{N}}\!=\!NF + F\cdot \qquad (176)$$

R = alkyl, aryl, perfluoroalkyl

The high efficiency of p-nitrosodimethylaniline as a scavenger for the hydroxyl radical (319) further demonstrates the affinity the nitroso group has for radicals.

9. Monoolefins

Both oxazetidines and copolymers are formed in reactions between perfluoroolefins and perfluoro nitroso derivatives (320) (equation 177). At lower temperatures polymer formation may predominate. Pyrolysis of the oxazetidinone from diphenylketene

$$CF_3CF_2NO \xrightarrow{CF_2=CF_2} CF_3CF_2\!-\!\underset{\underset{CF_2\text{-}CF_2}{|}}{\overset{\overset{O}{|}}{N}} + \left(\underset{\underset{CF_2CF_3}{|}}{O}\!-\!CF_2CF_2\right)_n \qquad (177)$$

and trifluoronitrosomethane gives both trifluoromethyl isocyanate and trifluoronitrosomethane (321) (equation 178). Apparently two oxazetidinones resulted from the combination

$$(C_6H_5)_2\underset{\underset{O\text{-}NCF_3}{|}}{\overset{|}{C}}\text{-}\underset{|}{C}{=}O \xrightarrow{300^{\circ}} CF_3NCO + CF_3NO \qquad (178)$$

of diphenyl ketene and nitrosobenzene. Pyrolysis of one gave benzophenone and phenyl isocyanate; the other was less stable and readily dissociated into carbon dioxide and benzophenone anil (322) (equations 179, 180);

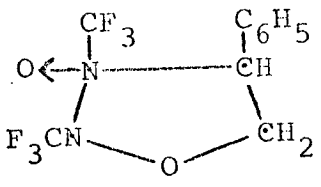
$$(C_6H_5)_2\underset{\underset{O\text{-}NC_6H_5}{|}}{\overset{|}{C}}\text{-}\underset{|}{C}{=}O \xrightarrow{\Delta} (C_6H_5)_2CO + C_6H_5NCO \qquad (179)$$

$$(C_6H_5)_2\underset{\underset{C_6H_5N\text{-}O}{|}}{\overset{|}{C}}\text{-}\underset{|}{C}{=}O \longrightarrow (C_6H_5)_2C{=}NC_6H_5 + CO_2 \qquad (180)$$

Trifluoronitrosomethane gives a 1:1 adduct with ethyl azodicarboxylate and both a 1:1 and a 2:1 adduct with styrene (321). The latter equimolar adduct undergoes pyrolysis with the formation of trifluoronitrosomethane, formaldehyde and the Schiff base of trifluoromethyl amine and benzaldehyde (equation 181). A 2:1 adduct obtained from

$$(CF_3NO)_2 + C_6H_5CH{=}CH_2 \xrightarrow{\Delta} C_6H_5CH{=}NCF_3 + CH_2O + CF_3NO \qquad (181)$$

trifluoronitrosomethane and trifluorostyrene (323) also releases trifluoronitrosomethane on heating. From n.m.r. data the first of the 2:1 adducts has been assigned the structure of a tetrahydro (1,2,3) oxadiazole (6) and the latter the structure of a 1,2-diazacyclobutane (7) (323).



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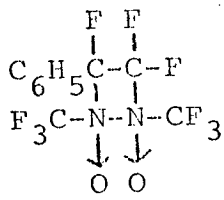

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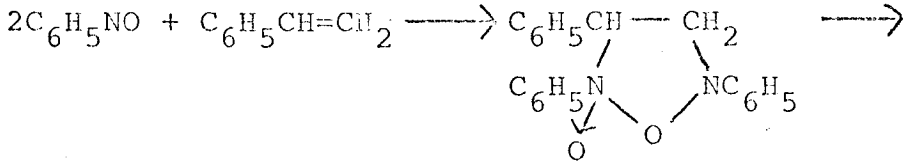
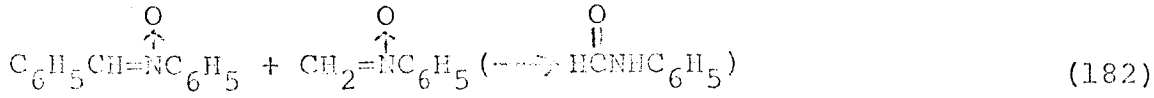
These adducts are structurally different from the adduct which has been obtained from nitrosobenzene and styrene and has been shown to be an unstable tetrahydrofuroxan which dissociates into nitrones (324) (equation 182).



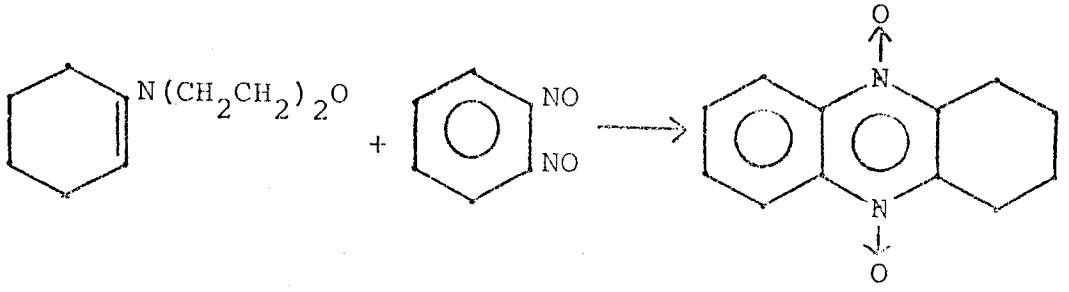


(182)

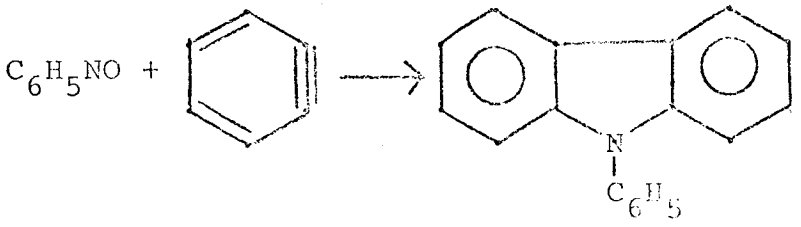
10. Acetylenes and arynes

Certain acetylenes combine with two moles of a nitroso compound to give vicinal bis-nitrones (325) (equation 183). A bis-nitrone, 1,2,3,4-tetrahydrophenazine-N,N'-dioxide is also obtained from 1-morpholinocyclohexene and o-dinitroso-benzene (benzfuroxan) (326) (equation 184). Other eneamines gave similar reactions. Nitrosobenzene adds to benzyne in a more complicated reaction which leads to the formation of N-phenylcarbazole (327) (equation 185).

$$C_6H_5C{\equiv}CC_6H_5 \xrightarrow{C_6H_5NO} (C_6H_5N(O){=}\overset{|}{C}C_6H_5)_2 \qquad (183)$$



(184)



(185)

11. Thioketones, phosphorous ylids, azomethine derivatives

Nitrosobenzene combines with a variety of doubly unsaturated bonds connecting carbon to a heteroatom (equations 186, 187, 188, 189), but it is not known whether or not these reactions proceed with the initial formation of four-membered rings (328, 329). The cleavage of nitrones by nitrosobenzene (equation 189) is apparently slow since nitrones are often prepared by reactions of nitroso compounds.

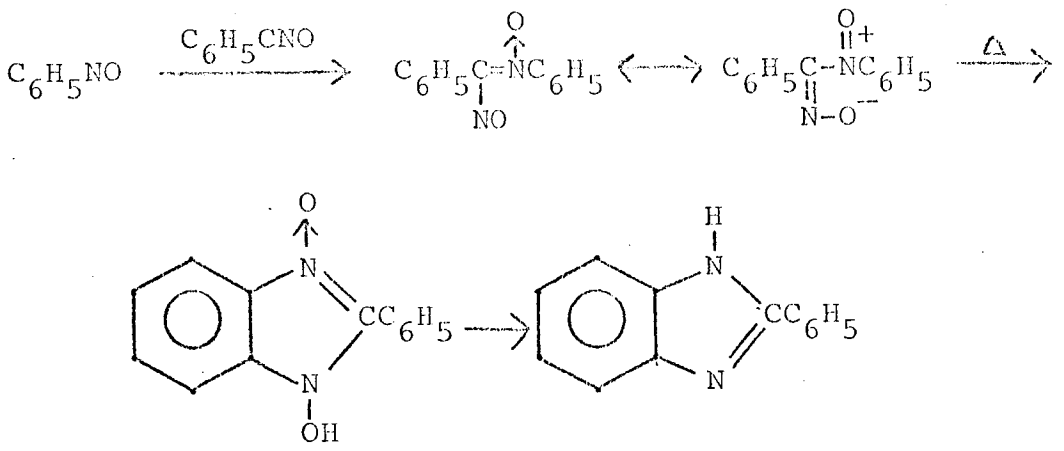
$$Ar_2C{=}S \xrightarrow{C_6H_5NO} Ar_2C{=}NC_6H_5 \qquad (186)$$

$$Ar_2\overset{+}{C}\text{-}P(C_6H_5)_3 \xrightarrow{C_6H_5NO} Ar_2C{=}NC_6H_5 \qquad (187)$$

$$(C_6H_5)_3P{=}N\text{-}N{=}C(C_6H_5)_2 \xrightarrow{C_6H_5NO} (C_6H_5)_2C{=}NC_6H_5 + N_2 + (C_6H_5)_3PO \qquad (188)$$

$$RCH(\overset{O}{\uparrow}){=}NC_6H_5 \xrightarrow{C_6H_5NO} RCHO + C_6H_5N(\overset{O}{\uparrow}){=}NC_6H_5 \qquad (189)$$

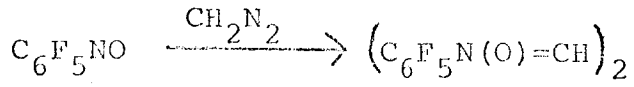
As a nucleophile, nitrosobenzene combines with benzonitrile oxide to produce a nitrosonitrone (330) (equation 190). On mild heating the latter cyclizes.



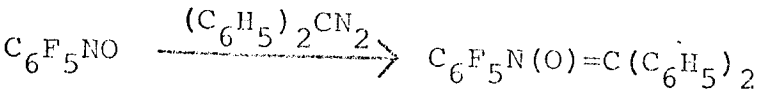
(190)

12. Diazoalkanes

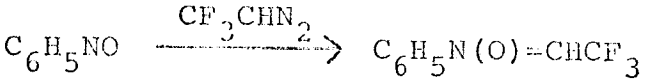
Many combinations of nitroso compounds and diazoalkanes lead to nitrones (331) (equations 191, 192, 193, 194). In the reaction with diazomethane oxidation may occur and the product is a bis-nitrone (equation 191). The same nitrone is obtained from the reaction between formaldehyde and phenylhydroxylamine and from the reaction between diazomethane and nitrosobenzene (332) (equation 195). It has been suggested that the reaction proceeds by electrophilic attack by nitroso nitrogen upon diazoalkane carbon (333). This is in agreement with the formation of an adduct between trifluoronitrosomethane and diazomethane which subsequently loses nitrogen (321). On treatment with diazomethane, the reduction of nitrosomesitylene to the corresponding hydroxylamine (334) may have proceeded with the initial formation of a nitrone followed by the Krȍhnke reaction, cf.C.18., in which the nitrone is cleaved to an aldehyde and a derivative of hydroxylamine.



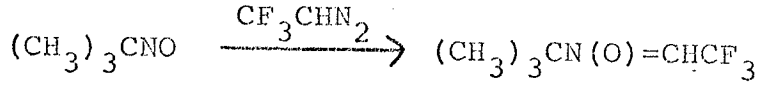
(191)



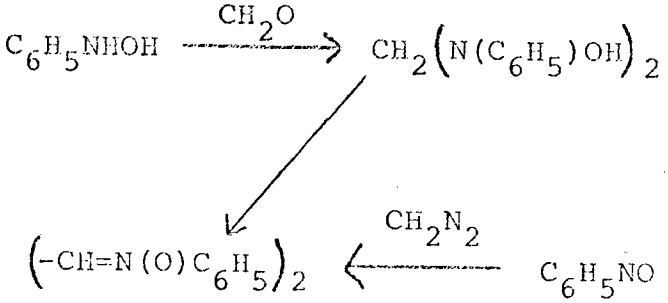
(192)



(193)



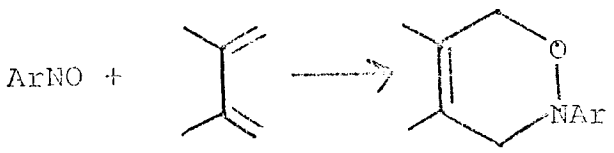
(194)



(195)

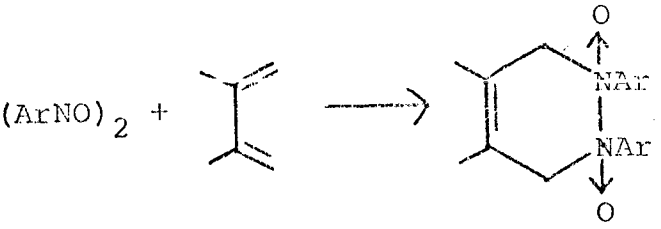
13. Conjugated dienes

Dihydro-1,2-oxazines are readily obtained from aromatic nitroso compounds and conjugated dienes. The addition of an aromatic nitroso compound to 2,3-dimethyl-1,3-butadiene follows first order kinetics in each reactant with low activation energies (14.23 kcal/mole for nitrosobenzene) (335) (equation 196).



(196)

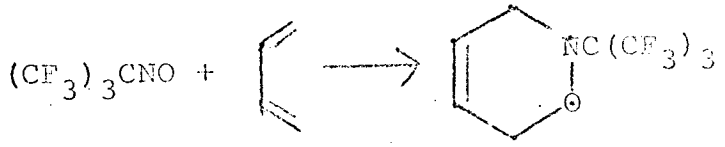
Nitroso dimers may combine with dienes with the formation of tetrahydropyridazine-N,N'-dioxides (336) (equation 197).



(197)

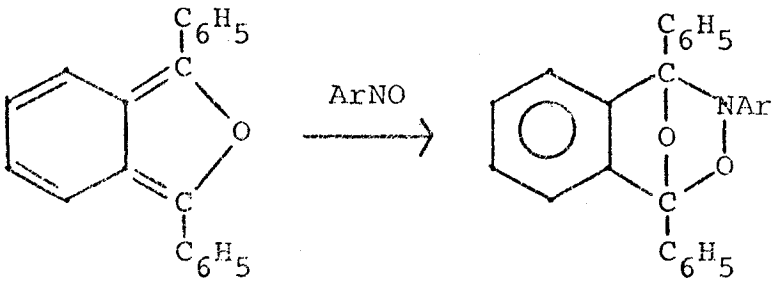
An unsymmetrically substituted diene may combine with a nitroso monomer to give a mixture of the two expected structural isomers (337). Apparently the monosubstituted 1-aryl-butadienes give exclusively the dihydrooxazines in which oxygen is attached to the benzylic carbon; the disubstituted 1-phenyl-4-carbomethoxy-butadiene gives the isomer in which nitrogen is attached to the benzylic carbon (338). Nitrosobenzene failed to react with anthracene (335).

Aliphatic nitroso compounds are more resistant to dienes; 2-methyl-2-nitrosopropane failed to react with 2,3-dimethyl-butadiene (339), however its perfluoroanalog combined with butadiene over a three day period in a sealed tube (340) (equation 198).



(198)

Both α-halo- and α-cyanonitrosoalkanes also combine with dienes to give the expected dihydrooxazine (339). The resistance of both 1-chloro-1-nitrosocyclohexane and nitrosobenzene to react with 2,3-diphenyl-, 1,1-diphenyl-, and 1,2,3,4-tetraphenylbutadiene -1,3 (341) may be attributed to a combination of steric and electronic effects but a steric hindrance does not prevent the addition of aromatic nitroso compounds to 1,3-diphenylisobenzofuran (342) (equation 199) or to tetraphenylcyclopentadienone (343).



(199)

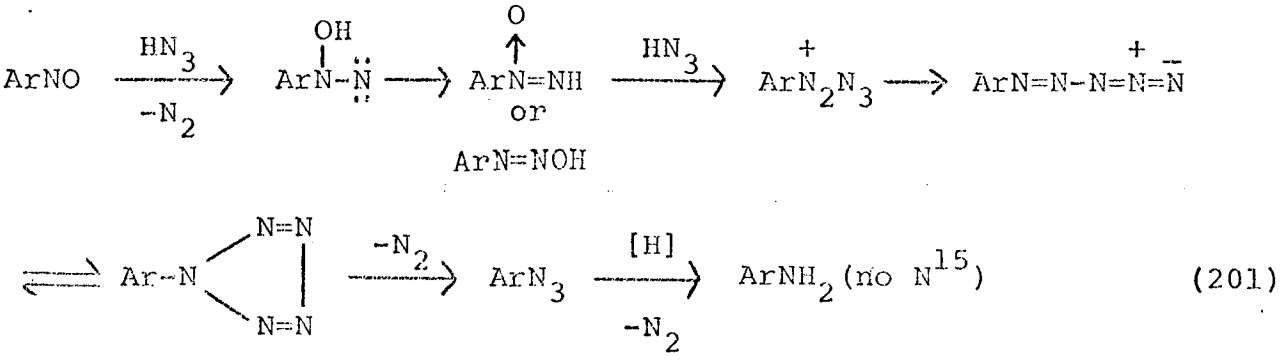
14. Compounds with active hydrogen

A compound which contains an active hydrogen may add in the expected manner to a nitroso group; diethyl acid phosphite adding to trifluoronitrosomethane gives an example (344) (equation 200). The nitroso group may also combine with

$$CF_3NO + (C_2H_5O)_2PHO \longrightarrow CF_3\underset{OH}{\overset{|}{N}}P(O)(OC_2H_5)_2 \qquad (200)$$

hydrogen azide. From aromatic nitroso compounds the corresponding aryl azides are often obtained in good yield. As expected,

electron withdrawing ring substituents facilitate the reaction. In support of both a linear and a cyclic pentazene intermediate (345), it has been shown by isotopic labeling that the two outer nitrogens in the product azide are derived from the outer nitrogens in hydrogen azide (equation 201). The reaction has been extended to the preparation of α-nitroazidoalkanes (346).



(201)

Nitrosobenzene is feebly basic (pKa $\simeq$ 0 at 25° in absolute methanol) (347); nevertheless, aliphatic and aromatic nitroso compounds are sufficiently nucleophilic to form adducts with p-toluene sulfinic acid (328) hydrogen chloride (348, 349, 350) and hydrogen bromide (349). Presumably the adducts are hydroxylamines (equation 202). In one instance a nitrosotoluene was transformed into a cresol by mineral acid conceivably by cleavage to a nitrosyl halide followed by diazotization of unchanged nitrosotoluene and hydrolysis (348) (equation 203). This agrees with the demonstration of the reversibility of nitrosation at carbon in which p-nitrosodimethylaniline was produced in an alcoholic hydrogen chloride solution of p-nitrosodiphenylamine and dimethylaniline (351). Concentrated sulfuric (352),

$$ArNO \xrightarrow{HX} ArN(X)OH \qquad (202)$$

$$ArNO \xrightarrow{HX} ArH + NOX$$

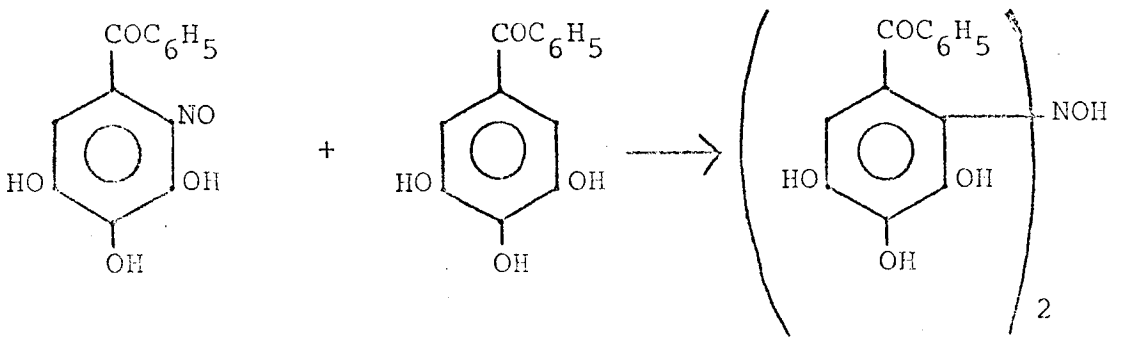
$$ArNO \xrightarrow{NOX} ArN_2X \xrightarrow{HOH} ArOH \qquad (203)$$

hydrofluoric (353) or peroxytrifluoroacetic (303) acid may catalyze an addition of nitrosobenzene to itself (equation 204). Similar

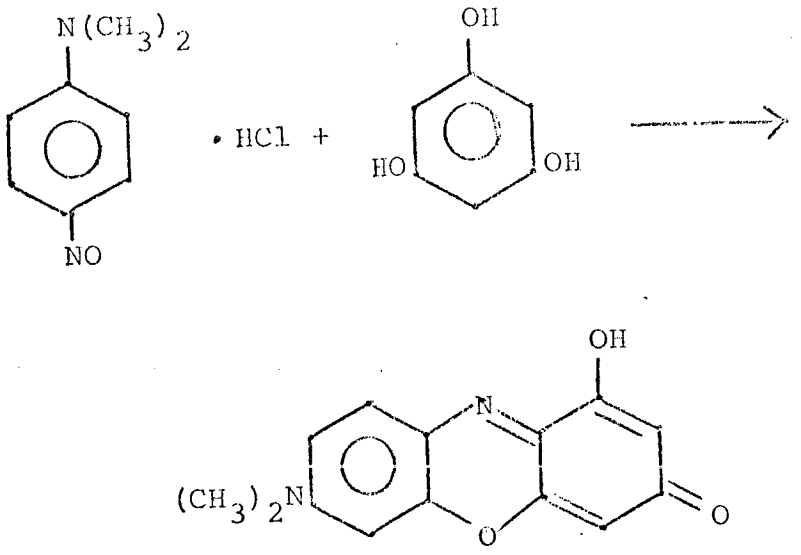
$$2C_6H_5NO \xrightarrow{acid} \underline{p}\text{-}ONC_6H_4N(C_6H_5)OH \qquad (204)$$

condensations occur with o- and m-substituted derivatives of nitrosobenzene (352), but more complicated reactions occur when a substituent is para to the nitroso group. From p-nitrosotoluene in concentrated sulfuric acid in acetic acid, dimethylphenazine oxide, dimethylphenazine, p-azoxytoluene, p-azotoluene and unidentified compounds are obtained (354).

Phenols combine with nitroso compounds with the generation of a new carbon-nitrogen rather than a new oxygen-nitrogen bond (355) (equations 205, 206). Ring-closure to phenoxazine derivatives may follow.

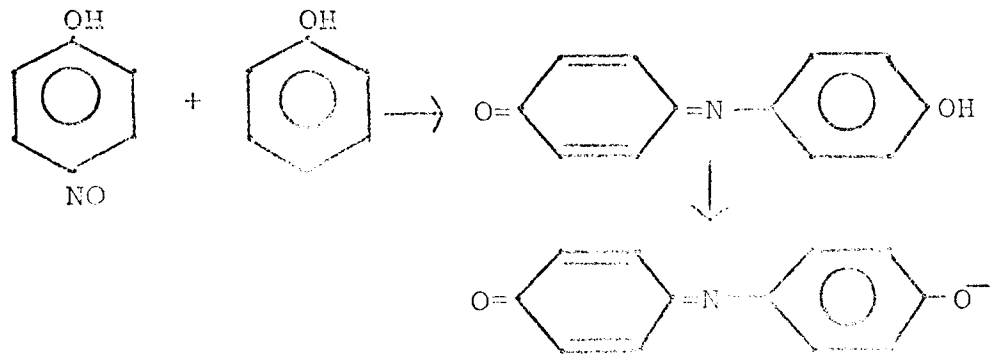


(205)



(206)

There are at least two condensations with phenols which have been developed in qualitative detection of the nitroso group. On treatment of a nitroso compound with a one percent solution of resorcinol in concentrated hydrochloric acid, a blue-violet color develops which after dilution with water, and extraction with ether, gives a red color (355a). In the other test, C-nitroso compounds, from which nitrous acid is eliminated upon treatment with concentrated sulfuric acid, give Liebermann's test with alkaline phenol. The nitrous acid reacts with the phenol to give p-nitrosophenol, which condenses with more phenol to give indophenol; when the product is poured into alkali, the blue color of the anion appears (355), (equation 206a).



(206a)

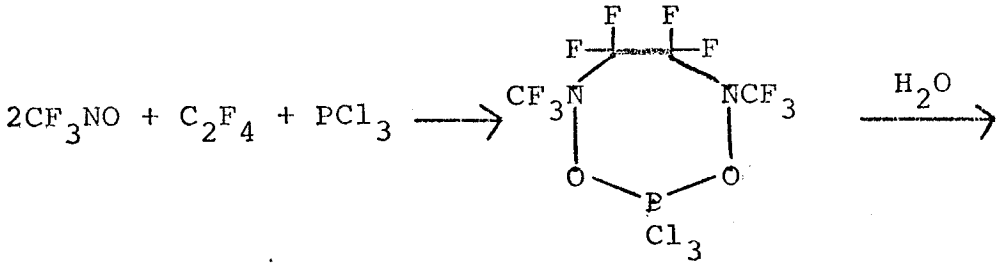
15. Complexes with metal salts and Lewis acids and metal chelates

Certain nitroso bases give colored precipitates of the corresponding ferro- and ferricyanide complexes. For example, p-nitroso-N,N-dimethylaniline ferrocyanide precipitates in red-brown needles which appear blue by reflected light (356). Sunlight irradiation of a potassium ferrocyanide solution with aromatic nitroso compounds first gives a red color followed by the formation of a complex salt with RNO of the type $K_3[Fe(CN)_5 \cdot RNO]$ (357). A similar exchange reaction between $Na_3[Fe(CN)_5NH_3]$ and RNO is brought about by sunlight and is accompanied by a color change from bright yellow to violet or green and has been used for the detection of aromatic nitroso compounds (358).

Complex salts from nitroso compounds and certain metallic halides have been noted in several instances. The green solution of nitrosobenzene, when mixed with an alcoholic solution of cadmium iodide, slowly deposits very small colorless crystals of the salt, $(C_6H_5NO)_5.CdI_2$ (359). With bismuth trichloride and p-nitroso-N,N-dimethylaniline, a similar complex, $2[p\text{-}NOC_6H_4N(CH_3)_2] \cdot 3BiCl_3$, is formed (360). Yellow amorphous complexes have been reported for $2C_6H_5NO \cdot SnCl_4$ and $2C_6H_5NO \cdot TiCl_4$ (361). By the direct addition of one mole of p-nitroso-N,N-dimethylaniline with one mole each of various uranyl salts in

suitable solvents, amorphous colored addition compounds are formed. For example, p-nitroso-N,N-dimethylaniline uranyl nitrate is amorphous, dark yellow and explosive; bis(p-nitroso-N,N-dimethyl-aniline) uranyl nitrate is orange-red and also explosive (362). Attempts to prepare similar salts from unsubstituted dimethylaniline failed.

A 1:1 adduct from nitrosobenzene and boron trichloride has been detected but not isolated (363) and a 2:1:1 adduct from trifluoronitrosomethane, perfluoroethylene and phosphorous trichloride has been isolated (364) (equation 207).

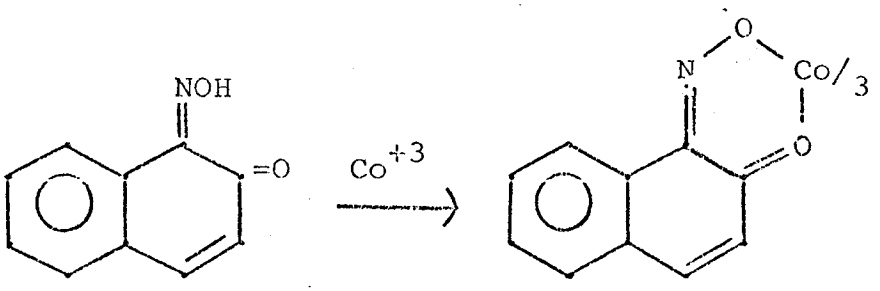


$$2CF_3NO + C_2F_4 + PCl_3 \longrightarrow \text{(adduct)} \xrightarrow{H_2O} H_3PO_4 + 3HCl + CF_3\underset{\underset{OH}{|}}{N}CF_2CF_2\underset{\underset{OH}{|}}{N}CF_3 \qquad (207)$$

A nitroso compound may be completely decomposed on shaking with mercury for a day (365) but nitrosoacetylenes and their mercury derivatives can be prepared from the corresponding mercury acetylides (366) (equation 208).

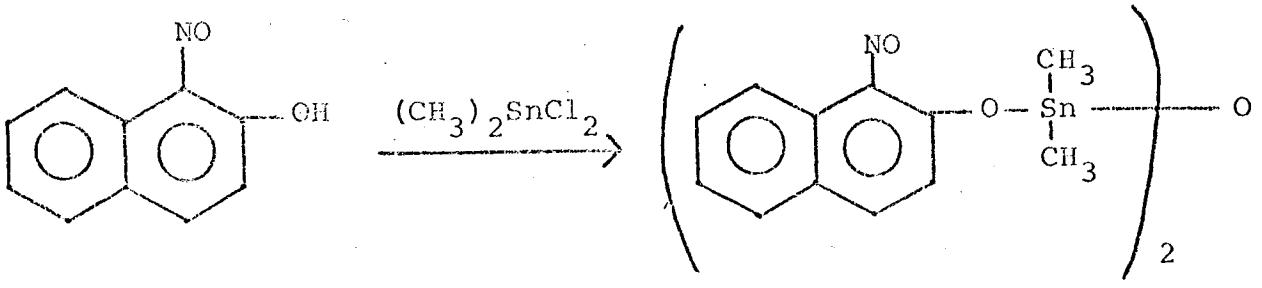
$$(C_4H_9C{\equiv}C)_2Hg \xrightarrow{NOCl} C_4H_9C{\equiv}CNO + (C_6H_9NOHg)_n \qquad (208)$$

Chelates of nitrosophenols and metal ions have been adapted to analytical procedures and are of wide importance in bonding metal dyes to fibers (367). The cobalt chelate of Gambine y (1-nitroso-2-naphthol) is a representative example (equation 209).



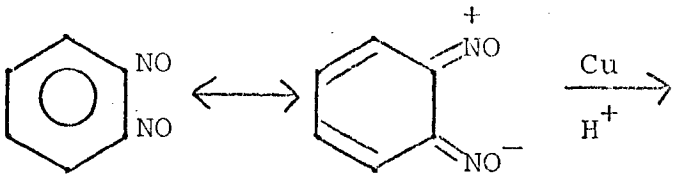
(209)

The same nitrosonaphthol combines with dialkyltin chlorides without chelating the nitroso group (368) (equation 210).

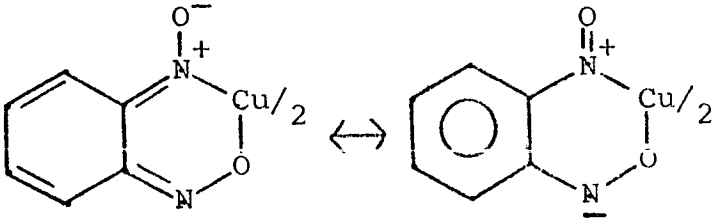


(210)

In the presence of acid, copper combines with the ring-opened isomer, o-dinitrosobenzene, of benzfuroxan (281) (equation 211).



(2 structures)



(211)

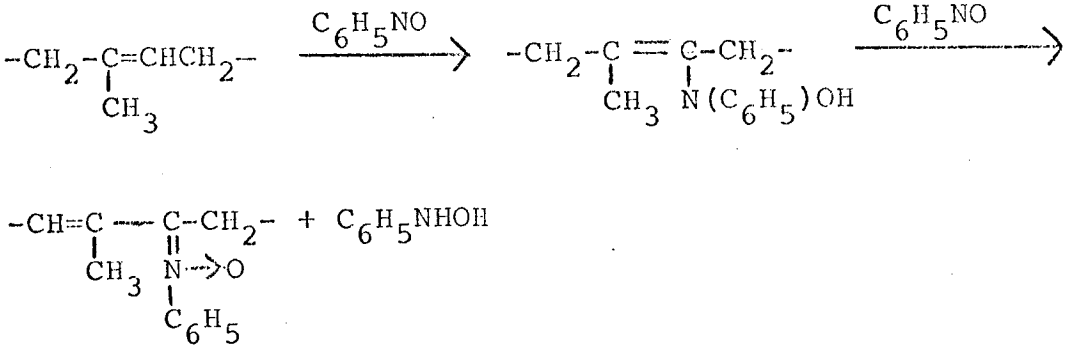
16. Terminal methylene groups

Certain olefins which do not combine with the nitroso group to give oxazetidines, cf.C.9, and have hydrogen attached to olefinic carbon may add to the nitroso double bond with the formation of an N,N-disubstituted hydroxylamine (323) (equation 212, 213). The reaction in which three molecules of

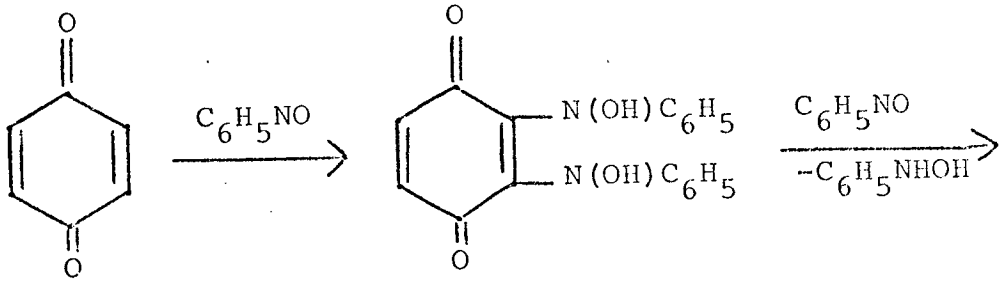
$$CH_2{=}CHCO_2CH_3 \xrightarrow{CF_3NO} CF_3\underset{\underset{OH}{|}}{N}CH{=}CHCO_2CH_3 \qquad (212)$$

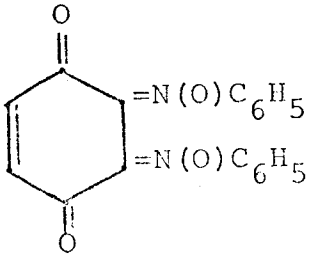
$$CH_2{=}CHOCOCH_3 \xrightarrow{CF_3NO} CF_3\underset{\underset{OH}{|}}{N}CH{=}CHOCOCH_3 \qquad (213)$$

nitrosobenzene combine with a C_5H_8 unit in rubber may require an initial addition of this kind with subsequent oxidation to a nitrone and azoxybenzene (369) (equation 214). The bis-nitrone obtained from nitrosobenzene and p-benzquinone (370) (equation 215) may also require initially the formation of a bis-hydroxylamine since azoxybenzene is also produced.



(214)





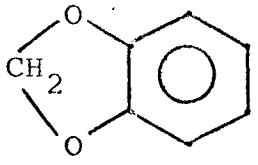
(215)

A similar attack by nitroso nitrogen on a terminal methylene group in an azomethine linkage has been described (371) (equation 216). Probably the base catalyzed addition of an aldehyde to the nitroso group is a related reaction (372) (equation 217). Safrole reacts with nitrosobenzene to give a

$$CH_2{=}NAr \xrightarrow{C_6H_5NO} C_6H_5\underset{\displaystyle OH}{\underset{|}{N}}CH{=}NAr \qquad (216)$$

$$RCHO \xrightarrow[Al(OR)_3]{ArNO} Ar\underset{\displaystyle OH}{\underset{|}{N}}COR \qquad (217)$$

nitrone and azoxybenzene; presumably the expected hydroxylamine is an intermediate (373) (equation 218).



$$\xrightarrow{C_6H_5NO} ArCH_2CH{=}CH\underset{\displaystyle OH}{\underset{|}{N}}C_6H_5 \xrightarrow{[O]}$$

$$ArCH{=}CHCH{=}\overset{\displaystyle O}{\overset{\uparrow}{N}}C_6H_5 + C_6H_5N{=}\overset{\displaystyle O}{\overset{\uparrow}{N}}C_6H_5 \qquad (218)$$

17. Grignard reagents

The early work of Wieland demonstrated the initial formation of an N,N-disubstituted hydroxylamine salt which subsequently may be reduced by an excess of the Grignard reagent to a secondary amine (374, 375) (equation 219). Hydroxylamines were

$$\text{ArNO} \xrightarrow{\text{Ar'MgBr}} \text{ArAr'NOMgBr} \xrightarrow{H_2O} \text{ArAr'NOH}$$

$$\text{ArAr'NOMgBr} \xrightarrow{\text{Ar'MgBr}} \text{ArAr'NMgBr} \xrightarrow{H_2O} \text{ArAr'NH} \qquad (219)$$

not isolated from nitrosobenzenes in which powerful electron-donating groups such as methoxy and dimethylamino occupied the para-position and further reaction leading to the expected secondary amine was detected (375) as well as reduction to corresponding azobenzenes (376). The formation of intermediate nitroso radical anions (377) appears probable but would not be required for the formation of p-tolylphenylnitric oxide from either p-nitroso-toluene with phenylmagnesium bromide or nitrosobenzene with p-tolylmagnesium bromide (378) (equation 220). Both dialkylzinc

$$\begin{array}{ccccc} \text{p-}CH_3C_6H_4NO & & & & \text{p-}CH_3C_6H_4MgBr \\ + & \longrightarrow & \text{p-}CH_3C_6H_4\overset{C_6H_5}{\underset{|}{N}}O & \longleftarrow & + \\ C_6H_5MgBr & & & & C_6H_5NO \end{array}$$

and alkyl Grignard reagents transform 2-halo-2-nitrosopropane into products of dehydrohalogenation, reduction and condensation (379).

18. Ehrlich-Sachs reaction

A base catalysed condensation between an active methylene group and the nitroso group attached to an aromatic ring is known as the Ehrlich-Sachs reaction (380). It is presumably initiated by a nucleophilic attack by the corresponding carbanion on nitroso nitrogen. Dehydration of an assumed intermediate hydroxylamine gives the expected product, an anil, in competition with oxidation to a nitrone (equation 221). Unreacted nitroso compound may serve as the oxidizing agent and is thereby reduced to an azoxy compound or an amine. The catalyst is usually provided by an aqueous alcoholic soda solution but sodium alkoxides (381, 382), alkali (383), piperidine (384) potassium cyanide, trisodium phosphate and other bases have been effective. In general the reaction leads to a mixture and there is limited success in predicting a predominance of dehydration or of oxidation product. Typical examples of compounds containing an active

$$>CH_2 \xrightarrow{OH^-} >CH^- \xrightarrow{ArNO} >\overset{\overset{Ar}{|}}{C}HN\text{-}O^- \xrightarrow[-OH^-]{H_2O}$$

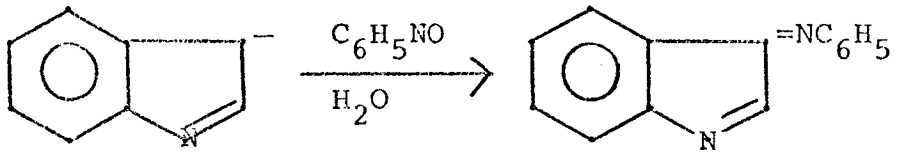
$$>CHN(Ar)OH \xrightarrow{-H_2O} >C{=}NAr \qquad (221)$$

$$\downarrow [O]$$

$$>C{=}N(O)Ar$$

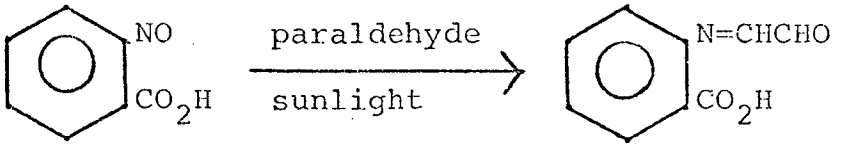
methylene group which participates in the Ehrlich-Sachs reaction include benzyl cyanide, 2,4-dinitrotoluene (384), certain cyclopentadienes (385), benzyldiphenylphosphine oxide (382), indole (386) and certain other heterocycles (387).

For an example of a postulated intramolecular condensation of an o-nitroso-N,N-dimethylaniline leading to the formation of the corresponding N-methylimidazole see B.22. In the condensation with indole the required anion is one expression of the resonance anion of indole (equation 222). An unidentified product,



(222)

$C_9H_7O_3N$, formed in the absence of base from paraldehyde and o-nitrosobenzoic acid exposed to sunlight may be the expected anil (388) (equation 223).



(223)

Benzyl and certain other halides also condense with aromatic nitroso compounds to give nitrones (383) (equation 224) by a reaction sequence in which initial attack by either a carbanion

$$ArCH_2Br \xrightarrow[OH^-]{Ar|NO} \begin{matrix} ArCHBr \\ Ar|N-O^- \end{matrix} \xrightarrow{-Br^-} \begin{matrix} ArCH \\ \| \\ Ar|N\rightarrow O \end{matrix} \qquad (224)$$

or a carbene seems plausible. Additional base is not requi: for the condensation between p-nitrosodimethylaniline and ethylene dibromide. The product, identical with the bis-nitrone obtained from p-nitrosodimethylaniline and diazomethane (389) (equation 225), cf.C.12., is transformed into bis-dimethyl-aminoazoxybenzene on being heated with p-nitrosodimethylaniline in ethanol. A preparation of aldehydes from nitrones by hydroly-

$$p\text{-}ONC_6H_4N(CH_3)_2 \xrightarrow[C_2H_5OH]{(CH_2Br)_2} \left((CH_3)_2NC_6H_4N(O)=CH\right)_2 \qquad (225)$$

sis (Kröhnke reaction) calls for a variation in the nitrone synthesis in which the halide is first transformed into its pyridinium salt (390).

Sulfonium ($R_2\overset{+}{S}-\overset{-}{C}R_2$) and phosphonium ylides readily combine with nitrosobenzene to give a nitrone and a sulfide in the former examples (391) (equation 226) and an anil and a phosphine oxide in the latter (328), cf.C.11.

$$Ar_2\overset{-}{C}-\overset{+}{S}(CH_3)_2 \xrightarrow{C_6H_5NO} Ar_2C=N(O)C_6H_5 + (CH_3)_2S \qquad (226)$$

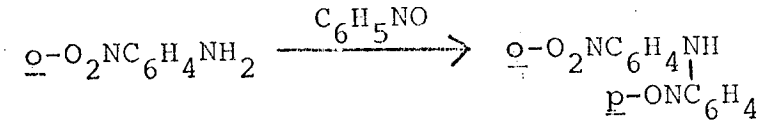
19. Amines, hydroxylamines, hydrazines

Amines, hydrazines and hydroxylamines are additional reagents which may attack the nitroso nitrogen. Azo compounds are formed in the condensation of primary aromatic amines with aromatic nitroso compounds generally carried out under mild conditions in acetic acid (392) (equation 227). Unsymmetrically substituted azo compounds are readily obtained; p-toluidine and nitrosobenzene or aniline and p-nitrosotoluene give nearly the theoretical amount of benzene-azo-p-toluene (393).

$$ArNO \xrightarrow[CH_3CO_2H]{Ar'NH_2} ArN{=}NAr' \qquad (227)$$

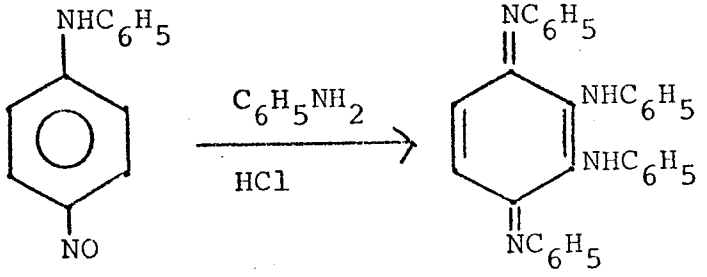
From a kinetic study a rate determining step in which protonated or acid-activated nitrosobenzene attacks nitrogen of free aniline in acetic acid has been postulated (394) with the recognition that a protonated N-anilinohydroxylamine may be an intermediate. Oxidation of the intermediate accounts for the formation of corresponding azoxy compounds as by-products (395).

In reaction with m- and p-nitroaniline, nitrosobenzene gives the expected azo compound; but o-nitroaniline combines with nitrosobenzene to give o-nitro-p'-nitrosodiphenylamine (392) (equation 228). It is reported that o-nitroaniline does not react with either o- or m- nitronitrosobenzene.



(228)

The condensation may lead to interesting variations as the following three reactions will illustrate. (1) An unidentified product, $C_{26}H_{18}ON_2$, was obtained from nitrosobenzene and α-naphthylamine (396). (2) Aniline condenses with each nitroso group in derivatives of p-dinitrosobenzene to give both the expected bis-azo- as well as the azoazoxy-products (397). (3) Azophenine is obtained on treating p-nitrosodiphenylamine with aniline in the presence of its hydrochloride (398) (equation 229).



(229)

There is a lack of information on possible reactions between primary aliphatic amines and nitroso compounds. Dilute aqueous ethyl amine reacts with 1-nitroso-2-naphthol to give 1-nitroso-2-N-ethylaminonaphthalene (399, 400) and no product was reported which would indicate a reaction at

the nitroso group. In general aromatic nitroso amines are produced by digesting nitrosophenols with hot solid ammonium chloride and ammonium acetate (401). Secondary amines may react in a complicated way with nitrosobenzene to give azobenzene, nitrobenzene, aniline and azoxybenzene. A small portion of the amine is changed into an N,N-dialkylhydroxylamine which also appears to be formed when nitrosobenzene is heated for a long time with a tertiary amine (402). It would appear that secondary amines are not highly reactive toward the nitroso group since piperidine is sometimes employed as a catalyst for other reactions. In concentrated sulfuric acid certain nitroso compounds and diphenylamine condense through the para-position to form highly colored blue quinonimines, sometimes used to detect the presence of a nitroso group (403).

Safranine, one of the earliest synthetic dyes, is a derivative of phenazine. A safranine dye may easily be obtained by heating p-nitroso-N,N-dimethylaniline with a primary aromatic amine in the presence of its hydrochloride (404).

Hydroxylamine will transform an aromatic nitroso compound into a diazonium hydroxide (400, 405). The reaction is probably catalysed by base and is limited to those nitroso derivatives which may not isomerize into oximes. As expected, many

nitrosopyrroles and nitrosophenols do not react in this way with hydroxylamine (406). On the other hand primary and secondary amino derivatives of aromatic nitroso compounds are more resistant to isomerization and are often diazotized by hydroxylamine. The transformation of p-anilinonitrosobenzene into p-anilinophenyl azide also demonstrates that an initially formed diazonium hydroxide may react further with hydroxylamine to form an azide (407) (equation 230).

$$p\text{-}C_6H_5NHC_6H_4NO \xrightarrow[OH^-]{H_2NOH} C_6H_5NHC_6H_4N_2^+OH^- \xrightarrow{H_2NOH} C_6H_5NHC_6H_4N_3 \qquad (230)$$

In the presence of hydroxylamine, β-nitroperfluoronitrosoethane is transformed into nitrodifluoroacetic acid (408) (equation 231), apparently by way of an intermediate diazonium compound.

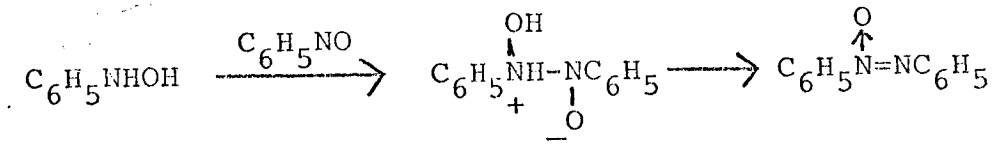
$$O_2NCF_2CF_2NO \xrightarrow[H_2O,\ <5^\circ]{H_2NOH} O_2NCF_2CF_2\overset{OH}{\underset{|}{N}}NHOH \xrightarrow{-H_2O} O_2NCF_2CF_2N{=}NOH \xrightarrow{-N_2} O_2NCF_2CF_2OH \xrightarrow{-HF} O_2NCF_2COF \xrightarrow{H_2O} O_2NCF_2CO_2H \qquad (231)$$

A condensation between an aromatic hydroxylamine and an aromatic nitroso compound leads to (an) azoxy compound(s) and may occur in acidic, neutral or basic solutions. From either p-chlorophenylhydroxylamine and nitrosobenzene or p-chloronitrosobenzene and phenylhydroxylamine, a mixture of all possible (four) symmetrically and unsymmetrically substituted azoxybenzenes are formed (409) (equations 232, 233). Apparently an equilibrium between each nitroso and hydroxylamino compound is present. In the condensation between nitrosobenzene and phenyl-

$$p\text{-}XC_6H_4NO + C_6H_5NHOH \rightleftharpoons p\text{-}XC_6H_4NHOH + C_6H_5NO \qquad (232)$$

$$\begin{matrix} p\text{-}XC_6H_4NO \\ C_6H_5NO \end{matrix} + \begin{matrix} p\text{-}XC_6H_4NHOH \\ C_6H_5NHOH \end{matrix} \longrightarrow \underset{\text{(4 products)}}{\overset{O}{\uparrow}\ ArN{=}NAr'} \qquad (233)$$

hydroxylamine in acid or neutral media, the rate is proportional to the concentration of each reactant and shows a variation with acid concentration. Two mechanisms proposed to fit the data (409) require (1) a reaction between free hydroxylamine and free nitrosobenzene in neutral media (equation 234) and (2) a condensation between phenylhydroxylamine and protonated nitrosobenzene in acidic media (equation 235). Either intermediate



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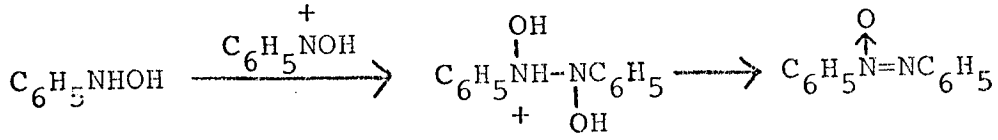


(235)

accounts for the rapid equilibration between substituted and unsubstituted nitroso and hydroxylamino compounds (equation 232) and for the loss of one-half of the isotope when one reactant is labeled with O^{18} (410). Each is consistent with the requirement for an intermediate with equivalent nitrogen atoms as demonstrated with the condensation between phenylhydroxylamine and nitrosobenzene containing N^{15} (411). In the latter example, azoxybenzene was monobrominated and reductively cleaved with the result that half of the isotope was found in aniline and half in p-bromoaniline.

Activation energies for corresponding condensations in acid or neutral media of nitrosobenzene with aniline (E_a 5.83 kcal/mole) and phenylhydroxylamine (E_a 10.8 kcal/mole) and activation entropies ($\Delta S^{\ddagger}$ -55.6 cal deg^{-1} $mole^{-1}$ for aniline and $\Delta S^{\ddagger}$ -32.5 cal deg^{-1} $mole^{-1}$ (estimated) for phenylhydroxylamine) reveal a higher order of reactivity for the aniline-nitrosobenzene reaction in agreement with a greater basicity of aniline over phenylhydroxylamine (pKa 5.804 for protonated

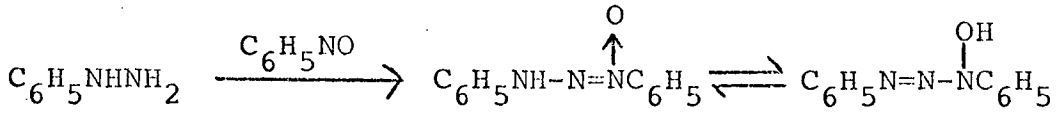
aniline and 3.462 for protonated phenylhydroxylamine in methanol at 25° (394)).

In the presence of certain bases nitrosobenzene and phenylhydroxylamine rapidly produce quantitatively nitrosobenzene anion radicals detected by e.s.r. Second-order kinetics for the decay of the radical anions is consistent with the following rapid equilibrium for the condensation in basic solution (412) (equation 236). It is particularly interesting that the nitrosobenzene radical anion is slowly formed in a solution of azoxybenzene in dimethyl sulfoxide 50% saturated with potassium hydroxide (412).

$$2C_6H_5NO\cdot \rightleftharpoons C_6H_5\overset{O^-}{\underset{O^-}{N-NC_6H_5}} \rightleftharpoons$$

$$C_6H_5\overset{O^-}{\underset{OH}{N-NC_6H_5}} \xrightarrow{-OH^-} C_6H_5N{=}N(O)C_6H_5 \qquad (236)$$

Apparently an expected adduct is readily formed on mixing a monosubstituted or an unsymmetrically di-substituted hydrazine with an aromatic nitroso compound. Dehydration to a triazene either does not occur or is insignificant and the predominant reaction for the intermediate is an oxidation to a triazene-N-oxide (413, 414) (equations 237, 238). A diarylamine is also



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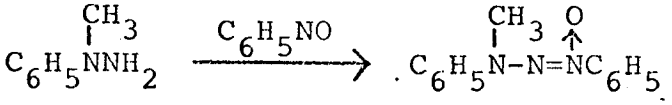
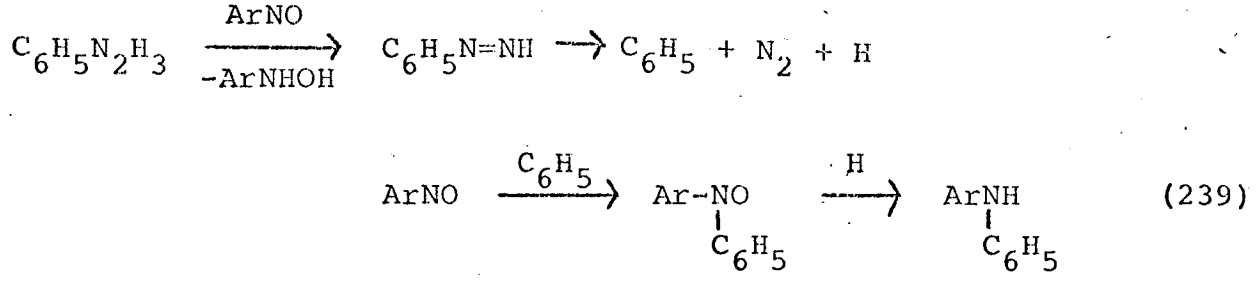


(238)

produced in certain condensations between an arylhydrazine and an aromatic nitroso compound. From isotope labeling it has been shown that the amine nitrogen is generated from the nitroso group (415). A possible explanation would require dehydrogenation to phenyldiimide and its decomposition to phenyl radicals. A diaryl nitroxide, produced by the combination of nitrosobenzene and phenyl, would then be reduced to a corresponding diaryl amine (equation 239). In support of the step requiring



(239)

dehydrogenation, it is known that nitrosobenzene combines with hydrazobenzene to give azobenzene and phenylhydroxylamine (416) (equation 240).

$$C_6H_5NO + (C_6H_5NH)_2 \longrightarrow C_6H_5N{=}NC_6H_5 + C_6H_5NHOH \qquad (240)$$

Semicarbazide combines with p-nitrosodimethylaniline to give the expected triazene-N-oxide (417) (equation 241) which is transformed into p-dimethylaminophenol on hydrolysis.

$$p\text{-}ONC_6H_4N(CH_3)_2 \xrightarrow{H_2NCONHNH_2} (CH_3)_2NC_6H_4\overset{\overset{O}{\uparrow}}{N}{=}N\text{-}NHCONH_2 \xrightarrow[H_2O]{H_2SO_4}$$

$$(CH_3)_2NC_6H_4OH + NH_3 + N_2 + CO_2 \qquad (241)$$

On mild heating in pyridine, chloramine-T reacts with nitrosobenzene to form an azoxysulfone (418) (equation 242) and may proceed either with the formation of an intermediate nitrene or by an addition and elimination sequence (419).

$$C_6H_5NO + p\text{-}CH_3C_6H_4SO_2N(Na)Cl \longrightarrow C_6H_5\underset{\underset{O}{\downarrow}}{N}{=}NSO_2C_6H_4CH_3 \qquad (242)$$

20. Substitution reactions in aromatic nitroso compounds

Substitution reactions of nitrosobenzene are unknown. Bromination (349) and nitration (420), which give p-bromo- and p-nitronitrosobenzene respectively, do not require ring-activation

through electron release from the nitroso group since they may proceed with the formation of intermediate hydroxylamine derivatives. An explanation for the catalysis of the bromination reaction by hydrogen bromide requires the initial formation of N-bromophenylhydroxylamine (349) (equation 243). In the absence of more definitive information a similar explanation based on the intermediacy of a phenylhydroxylamine derivative in the nitration reaction should be questioned. The reaction is carried out in carbon tetrachloride containing phosphorous pentoxide with dinitrogen pentoxide as the nitrating agent.

$$C_6H_5NO \xrightarrow{HBr} C_6H_5N(OH)Br \longrightarrow \underline{p}BrC_6H_4NHOH \longrightarrow$$

$$\underline{p}Br\text{-}C_6H_4N(OH)Br \xrightarrow{-HBr} \underline{p}Br\text{-}C_6H_4NO \qquad (243)$$

As an activator in nucleophilic displacement reactions of certain aromatic compounds, the nitroso group is more effective than the nitro group. In boiling sodium hydroxide solution 2,4-dinitrodimethylaniline is barely attacked whereas p-nitroso-dimethylaniline is hydrolyzed to give nearly quantitative yields of dimethylamine and quinone monoxime (421). Extension of this reaction to other p-nitroso-N,N-dialkylanilines provides

an important preparative method for pure secondary amines. Displacement of the alkoxy group in an alkyl ether of p-nitrosophenol may occur in a similar manner on treating the ether with a primary aromatic amine in the presence of acid (421a) (equation 243a) but p-nitrosophenol undergoes more complex changes. In the presence of aniline, it is transformed into

$$\underline{p}\text{-}ONC_6H_4OR \xrightarrow[-ROH_2^+]{ArNH_3^+} \underline{p}\text{-}ONC_6H_4NHAr \qquad (243a)$$

p-hydroxyazobenzene in acetic acid medium, into azophenine (cf. equation 229) in hydrochloric acid and into an indoaniline in strong sulfuric acid. A greater reactivity of p-bromonitrosobenzene in comparison with p-bromonitrobenzene toward silver nitrate has been described also as an illustration of the electron withdrawing power of the nitroso group (421).

Dipole moments and base-strengths provide additional evidence of the electron-withdrawing capacity of the nitroso group. The dipole moment of 3.2D for nitrosobenzene is reduced to 0.84D for p-nitronitrosobenzene (422). The large value of 6.9D for p-nitrosodimethylaniline which exceeds the vector sum, 4.8D, of the moments of dimethylaniline and nitrosobenzene has been ascribed to a contribution from a zwitterionic structure, cf.C.3., where the zwitterion itself would be expected to have a dipole moment in the order of 30D (423).

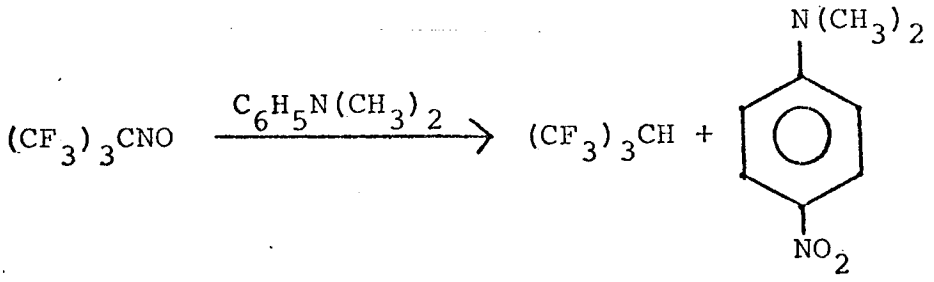
The zwitterionic structure for p-nitrosodimethylaniline may account for its otherwise unpredictably high base strength (pKa 4.0) (424) which is about one pK unit lower than that of N,N-dimethylaniline (pKa 5.15) (425). In marked contrast p-nitroaniline (pKa 1.11) (426) is a weaker base than aniline (pKa 4.62) (425) by over three pK units.

Resonance between the nitroso group and an attached aromatic ring would be reflected in a shortening of the C-nitroso bond. In p-iodonitrosobenzene this has been demonstrated in a C-nitroso bond of 1.28 Å, appreciably shorter than the C-N bond of 1.49 Å in aliphatic amines (427).

21. Cleavage of the C-nitroso bond

It has been suggested that initial nitrosation at carbon is reversible in nitrosative decarboxylation (equation 35) and that mineral acid may replace the nitroso group in a nitroso-toluene with hydrogen (equation 203). There are several other reactions in which cleavage of the C-nitroso bond occurs readily. Geminal dihalides may be prepared from corresponding nitrosochlorides and chlorine (428) (equation 244). At room temperature dimethylaniline in ether replaces the nitroso group in perfluoro 2-nitroso-2-methylpropane with hydrogen (428) (equation 245).

$$(CF_3)_2C(NO)Cl \xrightarrow{Cl_2} (CF_3)_2CCl_2 \qquad (244)$$



(245)

Pyrolysis of trifluoronitrosomethane and of pentafluoronitrosoethane has been assumed to proceed with initial cleavage of the C-nitroso bond (429) (equations 246, 247).

$$CF_3NO \xrightarrow{300^\circ} NO + CF_3$$

(Products isolated: $(CF_3)_2NOCF_3$, CF_3NO_2, $CF_2{=}NF$, (CF_2NF) and COF_2)

(246)

$$CF_3CF_2NO \xrightarrow{150^\circ} NO + CF_3CF_2$$

(Products isolated: CF_3NO_2, $CF_3N{=}NCF_3$, $(CF_3)_2NF$, CF_4,

COF_2 and nitrogen oxides) (247)

It should be noted that a molecular rearrangement is apparently required for the formation of the product, hexafluorodimethylamine, in the latter reaction. A similar cleavage in the mass spectrometer leads to the formation of the nitrosyl cation (NO^+) (429). Pyrolysis of geminal nitrosocyanides also proceeds with initial cleavage of the C-nitroso bond (430) (equation 248).

$$R_2C(NO)CN \xrightarrow[C_6H_5CH_3]{\text{reflux in}} \left(R_2\underset{CN}{C}\right)_2 NO\text{-}\underset{CN}{CR_2} \qquad (248)$$

The reversible photochemical dimerization of perfluoronitrosoalkanes cf.C.l., provides a classical example of the photolytic cleavage of the C-nitroso bond. In another example it is presumed that perfluoronitrosoethylene is initially formed in the irradiated mixture of perfluoroiodoethylene and nitric oxide which gives decomposition products (431) (equation 249). Irradiation of nitrosyl cyanide brings about dissociation into nitric oxide and cyanogen radicals (432).

$$CF_2{=}CFI \xrightarrow[h\nu]{NO} CF_2{=}CFNO \longrightarrow F_2CO + FCN + N_2 + NO_2 \qquad (249)$$

Following cleavage of the C-nitroso bond by irradiation, radical recombinations may bring about the formation of nitric

oxides which may be detected by e.s.r. and their subsequent transformation into trisubstituted derivatives of hydroxylamine (433) (equation 250).

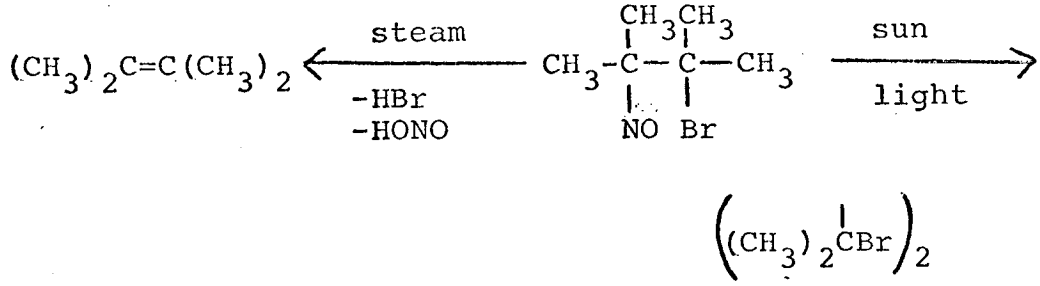
$$C_6H_5NO \xrightarrow{h\nu} (C_6H_5)_2NO$$

$$F_2C(NO)CF_2CO_2CH_3 \longrightarrow (CH_3O_2CCF_2CF_2)_2NO \qquad (250)$$

A photolytic elimination of nitrosyl hydride from certain nitrosoalkanes has been observed (434) (equation 251). It

$$(CH_3)_2\underset{\underset{NO}{|}}{C}CH_2CH_2CH(CH_3)_2 \xrightarrow[-NOH]{h\nu} (CH_3)_2C{=}CHCH_2CH(CH_3)_2 \qquad (251)$$

would appear that a similar elimination of nitrosyl bromide occurs as exposure to sunlight converts 2-nitroso-3-bromo-2,3-dimethylbutane into 2,3-dimethyl-2,3-dibromobutane (435) (equation 252). Elimination of the elements of nitrosyl bromide as both nitrous and hydrobromic acids occurs in boiling water (equation 252).

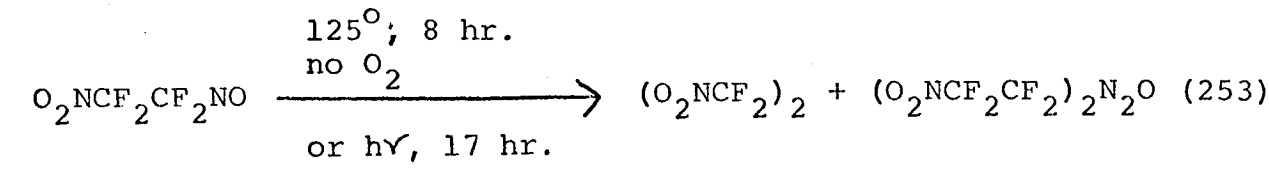


(252)

22. Pyrolytic and photolytic disproportionation

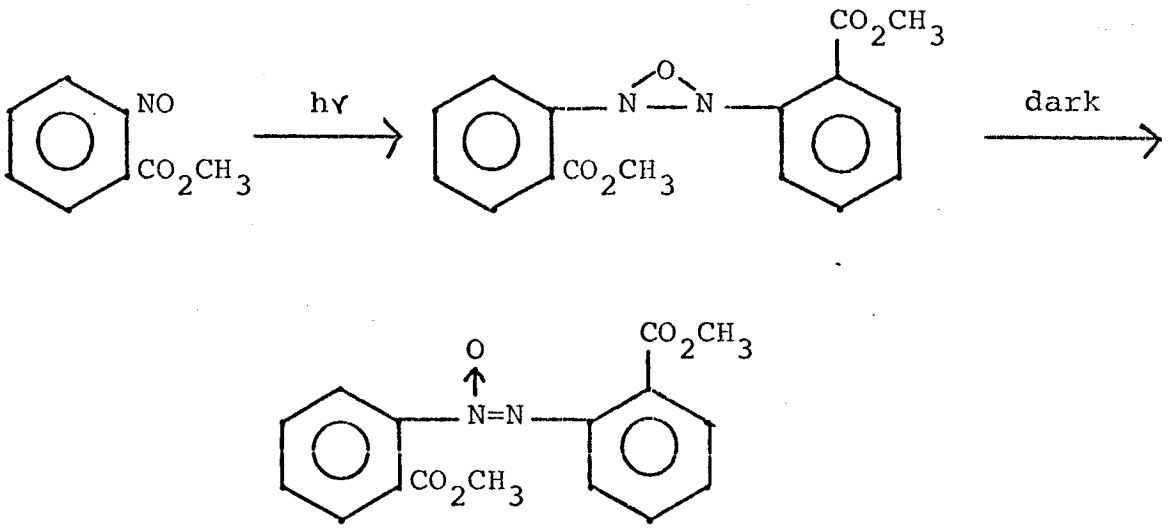
Bamberger first proposed that nitroso compounds may disproportionate with the simultaneous formation of a hydroxylamine and a nitro compound. On this basis he explained the formation of azoxybenzene, nitrobenzene, aniline, o-hydroxyazobenzene, o-hydroxyazoxybenzene, hydroquinone, p-hydroxyazoxybenzene and other products on exposing nitrosobenzene in benzene to sunlight. The same reaction(s) occur(s) more slowly in the dark or on heating nitrosobenzene in petroleum ether (436).

Disproportionation may lead directly to the formation of an azoxy and a nitro compound, the products obtained from both pyrolysis and photolysis of β-nitroperfluoronitrosoethane (437) (equation 253). Photolysis transforms methyl o-nitrosobenzoate



(253)

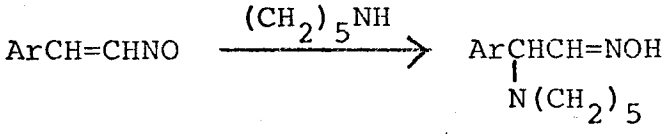
into the corresponding azoxy compound through an intermediate claimed to be the three-membered ring isomer of the azoxy compound (182) (equation 254). Methyl nitrobenzoate was not reported.



(254)

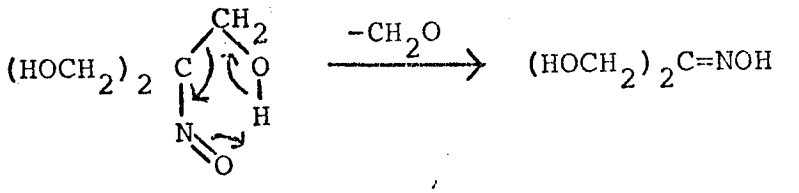
23. Miscellaneous reactions of nitroso compounds

a. Conjugate addition. Piperidine adds in the 1,4-manner to α,β-unsaturated nitrosoalkenes (438) (equation 255).



(255)

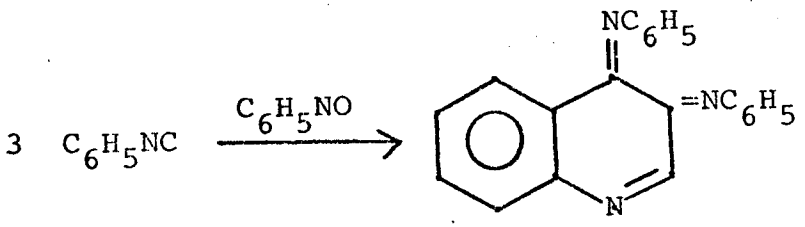
b. Fragmentation. On formation trihydroxymethylnitrosomethane dissociates into the oxime of dihydroxyacetone and formaldehyde (129). An appealing explanation calls for a redistribution of electrons in a cyclic transition state (equation 256) from which formaldehyde is eliminated. The reaction is reminiscent of decarboxylation of α-nitrosocarboxylic acids, cf.A.10.



(256)

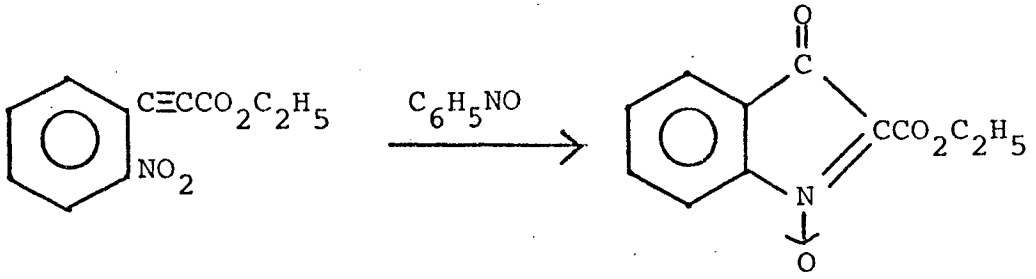
c. Reactions promoted by the presence of nitrosobenzene.

Trimerization of phenyl isocyanide in the presence of nitrosobenzene gives the dianil of 4-aza-1,2 naphthoquinone (439) (equation 257).



(257)

In the presence of nitrosobenzene, ethyl o-nitrophenylpropiolate undergoes isomerization with ring-closure (440) (equation 258).



(258)

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